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SATURATED δ-KETONIC ESTERS AND THEIR DERIVATIVES

BY DOROTHY A. HAHN AND ANGIE G. ALLBEE

In 1897 Vorländer[1] found that ethyl malonate combines with benzylidenacetophenone in the presence of sodium alcoholate, and that it is possible to get a saturated ketonic acid by hydrolyzing the product. Last year Kohler[2] showed that the addition product itself can be isolated in solid form if piperidine is used instead of sodium alcoholate as a condensing agent, and also that it is possible to use this addition product for getting unsaturated δ-ketonic acids. We undertook an investigation of the same reaction, but used anisyl styryl ketone with the expectation that this substance would give crystalline products that would be better adapted for a study of the isomerism that appeared in the unsaturated compounds.[3] As it will take a considerable time to complete the work with the unsaturated compounds, we thought it best to publish an account of the results that have been obtained with the saturated ketonic esters and their derivatives.

Malonic esters do not combine nearly so readily with anisyl styryl ketone as they do with phenyl styryl ketone. We first tried the condensation with sodium alcoholates, but found

[1] Ann. Chem. (Liebig), **294**, 332.
[2] THIS JOURNAL, **48**, 474.
[3] *Ibid.*, p. 476.

that while it was possible to show, by hydrolyzing the product, that some addition had taken place, it was not possible to isolate solid esters either with ethyl or methyl malonate. Better results were obtained with piperidine. After boiling an alcoholic solution containing equimolecular amounts of unsaturated ketone and ethyl malonate for seventy-two hours—the time that sufficed for complete addition to phenyl styryl ketone—we obtained a mixture of solids that, on separation, yielded about 20 per cent. of the possible amount of pure addition product, the remainder of the solid consisting mainly of unchanged ketone. The yield was increased by longer boiling, but the by-products also increased, and too prolonged heating resulted in a mixture that no longer solidified on cooling.

Diethyl (β-Anisoyl-α-phenylethyl)malonate, $CH_3OC_6H_4COCH_2CH(C_6H_5)CH(CO_2C_2H_5)_2$.—The best results were obtained by dissolving gram molecular quantities of the ketone and the ester in 200 cc. of absolute alcohol, adding 10 grams of piperidine, and boiling this solution continuously for six weeks. The product solidified upon cooling. After filtration and washing with alcohol, it was recrystallized from alcohol; this gave 200 grams of pure ester, a yield of about 50 per cent.

Analysis:

I. 0.1423 gram substance gave 0.3606 gram CO_2 and 0.0807 gram H_2O.

II. 0.1407 gram substance gave 0.3565 gram CO_2 and 0.0773 gram H_2O.

	Calculated for $C_{23}H_{26}O_6$	Found I	Found II
C	69.37	69.1	69.1
H	6.50	6.3	6.1

The ester is readily soluble in ether and hot alcohol. It separates from alcohol in coarse needles or plates melting at 78°.

Dimethyl (β-Anisoyl-α-phenylethyl)malonate, $CH_3OC_6H_4COCH_2CH(C_6H_5)CH(CO_2CH_3)_2$.—The unsaturated ketone combines more rapidly with the methyl than with the

ethyl ester of malonic acid, and it was found that the yield of pure product did not increase after boiling for three weeks. The procedure was as follows: Gram molecular quantities of unsaturated ketone and ester were dissolved in 150 cc. of methyl alcohol, 10 grams of piperidine added, and the solution was boiled continuously for three weeks. The solid product was filtered, washed with small quantities of methyl alcohol, and recrystallized from the same solvent. The yield in different experiments varied from 160 to 200 grams, 45 to 50 per cent. of the possible amount.

Analysis:

I. 0.1216 gram substance gave 0.3017 gram CO_2 and 0.0638 gram H_2O.

II. 0.1502 gram substance gave 0.3724 gram CO_2 and 0.0784 gram H_2O.

	Calculated for $C_{21}H_{22}O_6$	Found I	Found II
C	68.1	67.6	67.8
H	5.9	5.8	5.8

The methyl ester is much more easily separated from unchanged ketone than the ethyl ester. It is readily soluble in ether and in hot methyl alcohol, from which it separates in fine needles or plates melting at 104°.

(β-Anisoyl-α-phenylethyl)malonic Acid, $CH_3OC_6H_4COCH_2CH(C_6H_5)CH(CO_2H)_2$.—For the purpose of hydrolysis the ethyl ester was dissolved in alcohol and treated with an excess of concentrated aqueous potassium hydroxide. A crystalline potassium salt separated immediately. This was washed with alcohol, dissolved in a small quantity of water, and reprecipitated by addition of alcohol to the water solution. The salt crystallized from alcohol in fine needles or plates. Analysis:

I. 0.1033 gram substance gave 0.0411 gram K_2SO_4.

II. 0.1077 gram substance gave 0.0428 gram K_2SO_4.

	Calculated for $C_{19}H_{18}O_6K_2.H_2O$	Found I	Found II
K	17.88	17.83	17.88

These results show that the substance is the dipotassium salt of (anisoylphenylethyl)malonic acid. From a concen-

trated aqueous solution of the salt, acids precipitate the corresponding monopotassium salt, and this, in contact with excess of acid, slowly passes into the acid. The acid was purified by crystallization from ether or ethyl acetate.

Analysis:

I. 0.1227 gram substance gave 0.2993 gram CO_2 and 0.0568 gram H_2O.

II. 0.1451 gram substance gave 0.3548 gram CO_2 and 0.0663 gram H_2O.

	Calculated for $C_{19}H_{18}O_6$	Found I	Found II
C	66.6	66.5	66.6
H	5.2	5.1	5.2

(Anisoylphenylethyl)malonic acid crystallizes from water in fine needles containing water of crystallization which it loses below 130°. It is moderately soluble in hot water, but it is not feasible to recrystallize it from water, because, while dissolving, it slowly decomposes with evolution of gas. The acid melts with decomposition at about 165°. If the temperature is kept between 165° and 170° until the evolution of gas ceases, the loss in weight corresponds almost exactly to one molecule of carbon dioxide per molecule of acid.

1.0355 grams substance lost 0.1356 gram.

	Calculated for $C_{19}H_{18}O_6$	Found
CO_2	12.8	13.1

γ-Anisoyl-β-phenylbutyric Acid,

$CH_3OC_6H_4COCH_2CH(C_6H_5)CH_2CO_2H$.—The pale yellow liquid, obtained by heating (anisoylphenylethyl)malonate to 165°–170°, was poured, while still hot, into chloroform. From the chloroform solution ligroin precipitated a solid acid which was purified by recrystallization from ethyl acetate.

Analysis:

I. 0.1624 gram substance gave 0.4297 gram CO_2 and 0.0849 gram H_2O.

II. 0.1436 gram substance gave 0.3802 gram CO_2 and 0.0750 gram H_2O.

	Calculated for $C_{18}H_{18}O_4$	Found I	Found II
C	72.4	72.1	72.2
H	6.0	5.8	5.8

The acid is moderately soluble in hot ethyl acetate and chloroform, sparingly in ether, almost insoluble in ligroin. It separates from ethyl acetate in plates or prisms melting at 152°.

Methyl γ-Anisoyl-β-phenylbutyrate, $CH_3OC_6H_4COCH_2CH(C_6H_5)CH_2CO_2CH_3$.—The ester may be made by saturating a methyl alcoholic solution of the acid with gaseous hydrogen chloride, but it is more easily obtained by starting with the dipotassium salt of (anisoylphenylethyl)-malonic acid. For this purpose the salt is dissolved in water, the solution acidified with hydrochloric acid, and the resulting monopotassium salt immediately filtered, washed with small quantities of water and dried. The dried salt loses carbon dioxide at about 170°. The residue, while still hot, is poured into methyl alcohol and the solution saturated with hydrogen chloride. Potassium chloride is precipitated, and most of the ester separates in solid form when the solution cools. The remainder is readily obtained by concentrating the mother liquors. The ester was purified by recrystallization from alcohol, from which it separated in long plates or prisms melting at 86°.

Analysis:

I. 0.1539 gram substance gave 0.4098 gram CO_2 and 0.0879 gram H_2O.

II. 0.1268 gram substance gave 0.3381 gram CO_2 and 0.0719 gram H_2O.

	Calculated for $C_{19}H_{20}O_4$	Found I	Found II
C	73.0	72.6	72.7
H	6.4	6.3	6.3

The potassium salt of anisoylphenylbutyric acid was prepared by hydrolyzing the methyl ester. The ester was dissolved in alcohol, the solution treated with excess of strong alcoholic potassium hydroxide, and allowed to stand overnight at ordinary temperature. It was then slowly concen-

trated on a water bath until addition of ether to the cooled solution precipitated a crystalline potassium salt. This was purified by recrystallization from a mixture of alcohol and ether. It is readily soluble in alcohol, sparingly in ether, and crystallizes in minute needles or plates. Its water solution decolorizes potassium permanganate.

Analysis:

0.1082 gram substance gave 0.0270 gram K_2SO_4.

0.1047 gram substance gave 0.0263 gram K_2SO_4.

	Calculated for $C_{18}H_{17}O_4K.H_2O$	Found I	Found II
K	11.01	11.18	11.26

γ-Bromo-γ-anisoyl-β-phenylbutyric Acid, $CH_3OC_6H_4COCHBrCH(C_6H_5)CH_2CO_2H$.—Two isomeric bromine substitution products were obtained when bromine was added to a solution of anisoylphenylbutyric acid in chloroform. It was necessary to start the reaction by warming the solution, but after that the bromine disappeared as rapidly as added. As soon as one molecule of bromine had been added, part of the solvent was distilled. The residue, on cooling, deposited most of the product in the form of a colorless crystalline solid; the remainder was precipitated by addition of ligroin. The solid was washed with a small quantity of ether, then recrystallized from ethyl acetate. This deposited thin plates melting at 144° with evolution of gas.

The ethereal washings and the mother liquors yielded a second product, which was likewise recrystallized from ethyl acetate. After many recrystallizations it finally showed a constant melting point of 119°. The substance melts without decomposition but begins to give off gas a few degrees above the melting point.

Analysis:

I. 0.1664 gram substance (119°) gave 0.3503 gram CO_2 and 0.0719 gram H_2O.

II. 0.1202 gram substance (144°) gave 0.2535 gram CO_2 and 0.0509 gram H_2O.

	Calculated for $C_{18}H_{17}O_4Br$	Found I	Found II
C	57.3	57.4	57.5
H	4.5	4.7	4.7

The higher melting bromine compound is readily soluble in ethyl acetate and chloroform, moderately in ether, very slightly in carbon tetrachloride and ligroin. The lower melting compound is much more readily soluble in all solvents. Since both substances give the same lactone when treated with sodium carbonate, they must be stereoisomers. The higher melting product is obtained in much the largest quantity.

Methyl γ-Bromo-γ-anisoyl-β-phenylbutyrate, $CH_3OC_6H_4COCHBrCH(C_6H_5)CH_2CO_2CH_3$.—The methyl ester behaves like the acid toward bromine, and like the acid it gives two isomeric bromine substitution products. The reaction was carried out in chloroform. After removing most of the chloroform by distillation, hot methyl alcohol was added to the residue. The solution, on cooling, deposited hard plates that, after one crystallization from methyl alcohol, melted sharply at 122°.

The mother liquors, after concentration, deposited a second product in soft plates or needles that, after crystallization from methyl alcohol, melted at 84°. It was easy to get a complete separation of the two substances, and it was found that about 75 per cent. of the product was composed of the higher melting, the remainder of the lower melting substance. Both substances give the same products when hydrolyzed with potassium hydroxide.

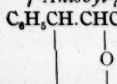
Analysis:

I. 0.1739 gram substance (84°) gave 0.3722 gram CO_2 and 0.0756 gram H_2O.

II. 0.1609 gram substance (122°) gave 0.3448 gram CO_2 and 0.0699 gram H_2O.

	Calculated for $C_{18}H_{18}O_4Br$	Found I	Found II
C	58.3	58.3	58.4
H	4.8	4.8	4.8

γ-Anisoyl-β-phenyl-γ-butyrolactone,



.—The two isomeric bromine substitution products of anisoylphenylbutyric acid behave in

exactly the same way when treated with sodium carbonate. The powdered acids dissolve readily in a cold dilute aqueous solution of the carbonate, the solution remains clear for a short time, then becomes milky, and in the course of half an hour the separation of lactone is complete. Both acids gave the same lactone. This was purified by recrystallization from alcohol or ethyl acetate, from which it separates in large six-sided prisms melting at 109°.

Analysis:

I. 0.1256 gram substance gave 0.3325 gram CO_2 and 0.0588 gram H_2O.

II. 0.1512 gram substance gave 0.4000 gram CO_2 and 0.0711 gram H_2O.

	Calculated for $C_{18}H_{16}O_4$	Found I	Found II
C	72.9	72.2	72.1
H	5.4	5.2	5.2

The lactone is moderately soluble in ether, readily soluble in alcohol, chloroform and ethyl acetate. The same lactone was obtained by hydrolyzing methyl anisoylbromophenylbutyrate, but when prepared in this way it was contaminated by a large quantity of by-products of which one was identified as anisoylphenylbutyric acid.

Diethyl (β-Bromo-β-anisoyl-α-phenylethyl)malonate, $CH_3OC_6H_4COCHBrCH(C_6H_5)CH(CO_2C_2H_5)_2$.—The bromine compound was prepared by adding a small quantity of bromine to a solution of the ethyl ester of (anisoylphenylethyl)malonic acid in chloroform, warming the solution until the reaction started, and then rapidly adding the calculated quantity of bromine. After the reaction had started the bromine disappeared as rapidly as it was added. The solvent was removed by distillation under diminished pressure, and the residue, while still hot, poured into alcohol. The alcoholic solution, on evaporation, deposited an oil that finally solidified when rubbed with a rod after standing for eight weeks. Only one of the two possible stereoisomeric products was isolated in solid form, but both were probably formed because the yield of solid product was only 25 per cent. of the possible amount

and the residual oil gave the same reactions as the solid. The solid was purified by recrystallization from alcohol.

Analysis:

I. 0.1680 gram substance gave 0.3573 gram CO_2 and 0.0802 gram H_2O.

II. 0.1332 gram substance gave 0.2838 gram CO_2 and 0.0636 gram H_2O.

	Calculated for $C_{28}H_{25}O_6Br$	Found I	Found II
C	57.8	58.0	58.1
H	5.2	5.3	5.3

The bromine compound is readily soluble in ether and alcohol. It separates from solution in large six-sided prisms melting at 97°. When treated with potassium hydroxide or sodium ethylate it readily loses hydrobromic acid and forms one or more unsaturated δ-ketonic esters. From the resulting esters, a variety of lactonic acids and both saturated and unsaturated lactones have been obtained; but as the relations between the isomeric substances have not yet been fully cleared up, this part of the investigation will be reserved for a later paper.

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[Contribution from the Massachusetts Agricultural College]

THE OXIDATION OF ALDEHYDES BY AN AQUEOUS SOLUTION OF BROMINE

By ERNEST ANDERSON

The standard method for converting aldose sugars into the corresponding acids is oxidation by an aqueous solution of bromine.[1] The opinion is prevalent that this method cannot be applied to the ordinary aliphatic and aromatic aldehydes. In order to test this point several aldehydes were treated with an aqueous solution of bromine and the oxidation products isolated. It was found as a result that some of the aldehydes, notably benzaldehyde, acetaldehyde, paraldehyde and formic acid, gave good yields of the corresponding oxidation products, benzoic, acetic and carbonic acids. Other aldehydes gave poor yields of the corresponding acids under the most favorable conditions. This was true of formaldehyde and aldol.

[1] Kiliani: Ber. d. chem. Ges., **17**, 1296.

Still other aldehydes, especially salicylaldehyde and chloral, gave no oxidation products at all. Salicylaldehyde appeared to go directly to tribromophenol while chloral was not attacked by the bromine. On the whole, the method is unsatisfactory, though by careful work it can be used.

The following table gives the amounts obtained, calculated as per cent. of the theoretical yield:

Substance	Acid formed	Yield in per cent.
Acetaldehyde	Acetic acid	71
Benzaldehyde	Benzoic acid	80
Paraldehyde	Acetic acid	86
Formic acid	Carbonic acid	80
Formaldehyde	Formic acid	poor
Aldol	β-Hydroxybutyric acid	poor
Salicylaldehyde	Salicylic acid	none
Chloral hydrate	Trichloroacetic acid	none

EXPERIMENTAL PART

Acetaldehyde.—A mixture of 37 grams of bromine and 25 cc. of water was added to a solution of 10 grams of acetaldehyde in 50 cc. of water. The contents of the vessel were kept at 8° C. during the mixing. The liquid bromine dissolved 15 minutes after mixing. The solution was left in the dark for 36 hours. Then the excess of bromine was removed by a slow stream of air. The hydrobromic acid was precipitated by the careful addition of silver carbonate. The slight excess of silver was precipitated by the addition of sodium carbonate solution. The alkaline filtrate was evaporated to dryness on the water bath. The salt residue was dissolved in a small amount of water, put into a distilling flask with excess of sulphuric acid and the acetic acid distilled over. The distillate, which consisted of water, acetic acid and traces of hydrobromic acid, was mixed with a concentrated solution of silver nitrate containing a slight excess of the salt for the aldehyde used. The silver bromide was filtered off and the silver acetate precipitated by the careful addition of sodium hydroxide to neutrality.[1] A yield of 27 grams of silver acetate

[1] When silver nitrate solution is added to hydrobromic and acetic acids, the silver bromide precipitates from acid solution. If the filtrate is then made just neutral with sodium hydroxide the silver acetate precipitates.

in three crops was obtained. This was purified by crystallization one time from water and gave the following results on analysis:

0.4163 gram salt, dried *in vacuo*, gave on ignition 0.2687 gram silver.

	Calculated for $AgC_2H_3O_2$	Found
Ag	64.67	64.52

The yield obtained is 71 per cent. of the theoretical. There are other products formed, among them one that affects the eyes. Probably the yield would be better if the solutions were more dilute during oxidation.

Paraldehyde.—A mixture of 19 grams of bromine and 50 cc. of water was added to a solution of 5 grams of paraldehyde in 750 cc. of water. The acetic acid was isolated from the oxidation mixture as in the case of acetaldehyde. A yield of 16.3 grams of silver acetate was obtained. This, after one crystallization from water, gave the following results on analysis:

1.3383 gram salt, dried *in vacuo*, gave on ignition 0.8623 gram silver.

	Calculated for $AgC_2H_3O_2$	Found
Ag	64.67	64.42

The yield is 86 per cent. of the theoretical. It could be easily raised to very near the theoretical. Apparently no other products are formed in this oxidation, but this point was not investigated.

Benzaldehyde.—A mixture of 9 grams of bromine and 25 cc. of water was added to 5 grams of benzaldehyde and 25 cc. water. The mixture was left at room temperature for 20 hours, then cooled in ice water and the benzoic acid filtered off. The air-dry substance weighed 3.3 grams and melted at 119° to 121° C. The filtrate was extracted three times with ether. The ether extract was shaken with silver carbonate to remove hydrobromic acid and bromine, and after drying over calcium chloride the ether was distilled off. The residual oil, consisting of benzaldehyde and benzoic acid, weighed 1.7 grams. This was separated by distillation into 0.4 gram

benzaldehyde boiling at 190° C., and 1.2 grams of benzoic acid melting at 118° to 120° C.

The yield is 80 per cent. of the theoretical. The 4.5 grams of benzoic acid, after one crystallization from water, melted at 120° to 121° C. and this melting point remained unchanged when the substance was mixed with chemically pure benzoic acid.

Formic Acid.—A mixture of 20 grams of bromine and 50 cc. of water was added to a solution of 5 grams of formic acid in 500 cc. of water. This solution was connected with a reflux condenser, to the upper end of which were connected four cylinders containing a saturated solution of barium hydrate. A slow stream of air, free of carbon dioxide, was drawn through the apparatus for 15 hours. Finally the formic acid solution was heated in the boiling water bath for 15 minutes to remove all the carbon dioxide. The barium carbonate was filtered off and weighed 26 grams, dried *in vacuo*. This is a yield of 80 per cent.

Formaldehyde.—Thirteen and two-tenths cc. of formalin solution containing 5 grams of formaldehyde were dissolved in 500 cc. water and oxidized with 57 grams of bromine. The carbon dioxide was determined as in the formic acid experiment. The barium carbonate weighed 31 grams. This is a yield of 94.2 per cent.

Repeated attempts were made to oxidize formaldehyde to formic acid with bromine. These always gave a small amount of formic acid which was isolated and analyzed as the lead salt.

One hundred cc. of formalin solution, corresponding to 38 grams of formaldehyde, were dissolved in 900 cc. of water and 195 grams of bromine added. After standing 24 hours the hydrobromic acid was removed by lead carbonate and afterwards by silver carbonate. The lead and silver were precipitated by hydrogen sulphide. The dissolved hydrogen sulphide was removed by heating the solution. The formic acid was isolated by treating the solution with lead carbonate on the boiling water bath, filtering and concentrating *in vacuo*. This gave 35 grams of lead formate which, on crystallization

from water and drying *in vacuo*, gave on analysis the following result:

0.9565 gram substance, on precipitation as the carbonate and ignition, gave 0.7213 gram lead oxide.

	Calculated for $Pb(CHO_2)_2$	Found
Pb	69.7	70.0

Aldol.—A mixture of 70 grams of bromine and 50 cc. water was added to a solution of 36 grams of aldol in 350 cc. of water. The solution became quite warm and considerable oil separated out. After standing 18 hours, the solution was extracted three times with ether to remove the oil. This ether extract gave 15.6 grams thick, dark gum insoluble in water and affecting the eyes badly, which was finally thrown away.

The water solution was treated with silver carbonate to remove hydrobromic acid. The silver was precipitated as silver sulphide and the water distilled off *in vacuo*. The oil was taken up in ether and found to weigh 23 grams. This was treated first with silver carbonate and afterwards with a strong solution of silver nitrate. The solution, which was acid, was made almost neutral by the addition of sodium hydroxide and concentrated *in vacuo*. On the addition of alcohol, 36 grams of crystalline salt, in two crops, were obtained. This was purified by dissolving in 150 cc. boiling water, filtering and adding 300 cc. alcohol. On analysis the pure salt gave the following result:

0.8062 gram substance, dried *in vacuo*, gave on ignition 0.4133 gram silver.

	Calculated for $AgC_4H_7O_3$	Found
Ag	51.19	51.26

The salt showed all the properties of silver β-hydroxybutyrate described by Wurtz.[1]

Salicylaldehyde.—This substance gave a very large amount of tribromophenol and no salicylic acid when it was treated in aqueous solution with bromine.

[1] Jahresbericht, **1870**, 657; **1872**, 449; **1873**, 473.

Chloral Hydrate.—It was found impossible to oxidize this substance in aqueous solution with bromine.

[Contributions from the Sheffield Laboratory of Yale University]

CCV.—RESEARCHES ON PYRIMIDINES

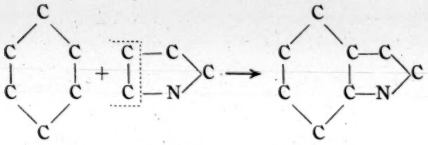
BARBITURYL- AND 2-THIOBARBITURYL-5-ACETIC ACIDS

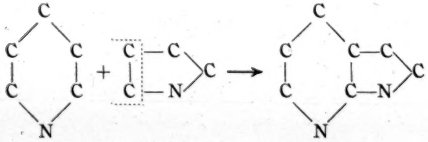
By Treat B. Johnson and Edward F. Kohmann

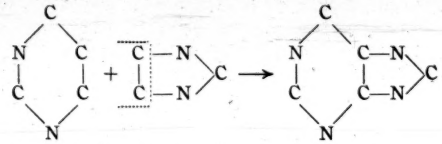
[FIFTY-NINTH PAPER]

The imidazoles, pyrroles, pyrimidines and pyridines are types of heterocyclic combinations which are of common occurrence among natural substances. These nitrogen cycles functionate in nature's processes not only in their simple forms, but also as condensed nuclei which retain, to a certain degree, the characteristic properties of the simple cycles. For example: Not only do we find the two heterocycles, imidazole and pyrimidine, represented by the amino acid histidine, the Jaborandi alkaloids pilocarpine, isopilocarpine and pilocarpidine,[1] ergothioneine,[2] uracil, thymine and cytosine, but we also find representatives of condensed nuclei of these two rings, the purines (III), widely distributed in both animal and vegetable organisms. The pyrrole compounds are not only found as such in the blood, proteins and chlorophyll of plants, but also in the form of condensed nuclei of this ring with benzene, the indoles (I). This type of nitrogenous compounds is represented by the amino acid tryptophane, and its betaine derivative hypophorine,[3] indigo, skatole and indole. Closely related to the indoles are the corresponding pyridine derivatives, the *pyrindoles* (II), which contain condensed pyridine and pyrrole nuclei. For our present knowledge of this new class of substances we are indebted to Perkins.[4] He has shown that their structure affords an explanation of the unique reactions of the naturally occurring alkaloids, harmine and harmaline.

[1] Pictet and Biddle: Vegetable Alkaloids, p. 171.
[2] Tanret: J. pharm. chim., **30,** 145. Barger and Ewin: J. Chem. Soc., **1911,** 2336.
[3] Centralb., **1911,** I, 1548.
[4] W. H. Perkins and R. Robinson: J. Chem. Soc., **101,** 1775.



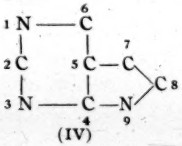




So far as the writer is aware, substances containing condensed pyrimidine and pyrrole nuclei, corresponding to the indoles (I) and pyrindoles (II), represent new types of organic compounds concerning which we have no knowledge. It is therefore of especial interest and desirable to develop methods for their synthesis and investigate their chemical behavior. Such combinations would not only be of physiological interest, but it is also not improbable that such heterocyclic substances may be found to occur in nature. We shall record therefore, in this paper, some results of attempts to obtain representatives of this new class of compounds.

As the nomenclature of compounds containing condensed pyrimidine and pyrrole nuclei presents some difficulties we shall call such substances *pyrimazoles*. Furthermore, since there are three structurally isomeric forms theoretically possible,

depending upon the position occupied by the pyrrole nitrogen in the condensed nucleus, we shall designate them as 1,3,9- 1,3,7- and 1,3,8-pyrimazoles, as represented by Formulas (IV), (V) and (VI), respectively. The method of numbering the different positions in the ring is analogous to that adopted in the purine series. The numbers before the name *pyrimazole* indicate the positions occupied by the nitrogen atoms in the heterocycle.



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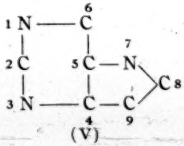

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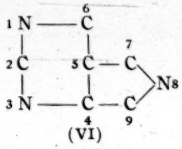
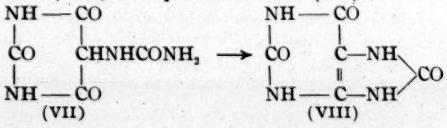
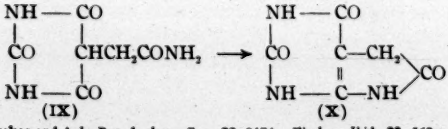


(VI)

Two methods of synthesizing 1,3,9-pyrimazole compounds (IV) which seemed feasible were the following: (1) To prepare a 4- or 6-aminopyrimidine derivative of acetic acid or its ester and then condense to a γ-lactam ring with formation of an oxypyrimazole. (2) To synthesize the amide of barbituryl-5-acetic acid (IX), and then condense this to a pyrimazole (X), with formation of water. A condensation of this nature would be perfectly analogous to that involved in the formation of uric acid (VIII) from pseudouric acid[1] (VII).



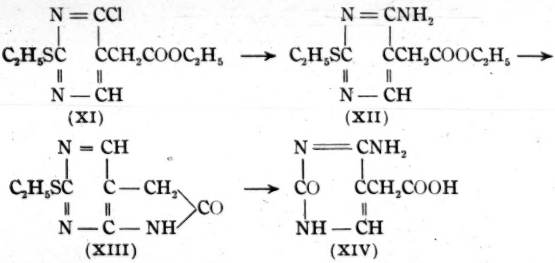
(VII) (VIII)



(IX) (X)

[1] Fischer and Ach: Ber. d. chem. Ges., **28**, 2474. Fischer: *Ibid.*, **30**, 560.

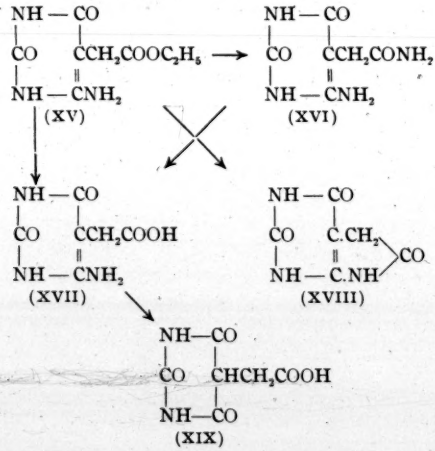
A synthesis of Type 1 has already been applied successfully, and the pyrimazole derivative obtained has been described in a previous paper from this laboratory.[1] It was prepared by heating ethyl 2-ethylmercapto-6-chloropyrimidine-5-acetate (XI) with ammonia. The chlorine atom was displaced by the amino group by this treatment, and the corresponding aminopyrimidine (XII) was formed. This compound then underwent a lactam condensation with evolution of alcohol and formation of the mercaptopyrimazole (XIII). This substance was named 2-ethylmercapto-5,6-(α-pyrolidone)-pyrimidine, but according to our proposed nomenclature it would be called 2-ethylmercapto-8-oxy-1,3,9-pyrimazole. This compound possessed properties of a γ-lactam and consequently underwent hydrolysis when warmed with hydrochloric acid, forming quantitatively cytosine-5-acetic acid (XIV) with evolution of ethyl mercaptan.



In order to determine whether pyrimazoles can be obtained by application of this reaction in other cases, we have now investigated the behavior of diethyl α-cyanoethane-α,β-dicarboxylate[2] towards urea. Theoretically this ester would be expected to condense in a manner analogous to that of ethyl cyanoacetate, forming ethyl 2,6-dioxy-4-aminopyrimidine-5-acetate (XV) We now find that this ester does not enter into a smooth reaction with urea, and that the greater proportion of both reagents undergo decomposition when digested

[1] Johnson: J. Am. Chem. Soc., **33**, 758.
[2] Haller and Barthe: Ann. chim. phys., [6] **18**, 283.

together in the presence of sodium ethylate. The results which we obtained showed, however, that a portion of the carboxylate condenses normally, forming the pyrimidine (XV), as expected. This compound was not isolated, but its primary formation was established by the fact that ammonia and barbituryl-5-acetic acid (XIX) were formed when the crude reaction product was digested with hydrochloric acid. Part of the ester undergoes saponification during the digestion, giving the corresponding acid (XVII), part combines with ammonia, forming apparently the amide (XVI), and it also undergoes an inner condensation as expected, forming 2,6,8-trioxy-1,3,9-pyrimazole (XVIII). The yields, however, of these pyrimidines were variable and it was impossible to so control the conditions of the reaction that the pyrimazole could be obtained in large amounts. The pyrimazole was obtained as a light colored powder, which was insoluble in water, and possessed no definite melting point. The amide was not isolated in a pure condition. These various changes are represented by the following structural formulas:



Pseudouric acid (VII) easily undergoes an inner condensation with formation of uric acid[1] when heated with oxalic or hydrochloric acids. Fischer[2] was unable, however, to effect an analogous condensation with 6-thiopseudouric acid. 2-Thiopseudouric and 2-thiouric acids have not been synthesized.[3] These pseudouric acids are closely related in structure to the amides of barbituryl- and 2-thiobarbituryl-5-acetic acids, (XXV) and (XXVI), and consequently it seemed of interest to prepare the latter and determine whether they would undergo a condensation analogous to that of the pseudouric acids, giving the corresponding 1,3,9-pyrimazoles, (XXVIII) and (XXIX). They were obtained by condensation of triethyl ethane-α,α,β-tricarboxylate[4] (XXII) with urea and thiourea, respectively. By the action of this ester on these ureas we expected to obtain the corresponding esters, (XXIII) and (XXIV), and then convert these into their corresponding amides by the action of ammonia. To our surprise, however, the amides were formed in one operation because of the fact that part of the ureas underwent decomposition with formation of ammonia. This then reacted with the esters in alcohol, giving the corresponding amides. Barbituryl-5-acetamide (XXV) was obtained in the form of its sodium salt, which was difficultly soluble in cold water and contained 4 molecules of water of crystallization. Thiourea condensed with the tricarboxylate, giving the corresponding salt of the sulphur pyrimidine, which separated in an anhydrous condition. Both salts dissolved in warm water and on acidifying their respective solutions the amides (XXV) and (XXVI) were obtained.

The ease with which these two esters react with ammonia, forming the amides (XXV) and (XXVI), is remarkable and of especial interest, because it has been our previous experience that esters of pyrimidine acids react with difficulty with ammonia. For example, in order to prepare 2-ethylmercapto-6-oxypyrimidine-5-acetamide (XX) from the corresponding

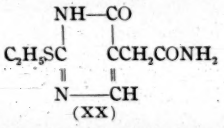
[1] Fischer and Ach: *Loc. cit.*

[2] Fischer and Ach: Ann. Chem. (Liebig), **288,** 157.

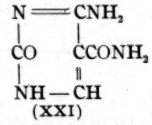
[3] Richter's Lexikon der Kohlenstoffverbindungen.

[4] Wislicenus and Nassauer: Ber. d. chem. Ges., **27,** 797. Bischoff: Ann. Chem. (Liebig), **214,** 38.

ester it was necessary to heat this with ammonia at 140°–150°[1] while, on the other hand, it has been shown that 5-carbethoxycytosine exhibits a remarkable inertness and can not be converted into its corresponding amide (XXI) when heated with ammonia under similar conditions.[2]

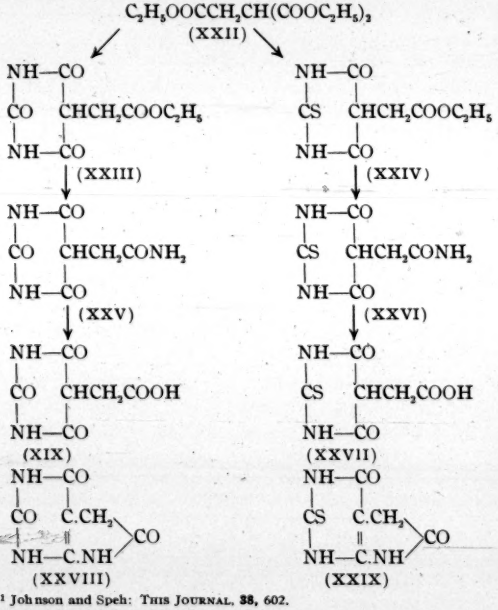


(XX)



(XXI)

Attempts to condense the two amides (XXV) and (XXVI) to the corresponding pyrimazoles were unsuccessful. They were



[1] Johnson and Speh: THIS JOURNAL, **38**, 602.
[2] Wheeler and Johns: *Ibid.*, **38**, 594; **40**, 233.

easily decomposed by the action of alkali and hydrochloric acid and underwent hydrolysis, with formation of the corresponding acids, viz., barbituryl-5-acetic (XIX) and 2-thiobarbituryl-5-acetic acids (XXIX), respectively.

EXPERIMENTAL PART

The Condensation of Urea with Triethyl Ethane-α,α,β-tricarboxylate, $C_2H_5OOCCH_2CH(COOC_2H_5)_2$

Barbituryl-5-acetamide, — This acid amide was obtained in the form of its sodium salt by digesting urea with triethyl ethane-α,α,β-tricarboxylate in alcohol and in the presence of sodium ethylate. The method of procedure was as follows: Two molecular proportions of sodium (3.4 grams) were dissolved in 75 cc. of absolute alcohol and a molecular proportion of urea (4.4 grams) dissolved in the alkaline solution. Eighteen grams of the tricarboxylate were then added at once, when there was an immediate reaction and a colorless salt separated. The mixture was then heated on a steam bath for about 10–11 hours in order to complete the reaction. The alcohol was finally evaporated and the residue triturated with about 20 cc. of cold water and a little ether, when we obtained the sodium salt of the amide as a colorless crystalline powder. The yield was 6.9 grams. We obtained no precipitate when the aqueous filtrate was acidified with acetic or hydrochloric acids. This sodium salt is insoluble in alcohol, but crystallizes from hot water in slender, colorless prisms arranged in rosettes which have no definite melting or decomposition point. The salt contained four molecules of water of crystallization, which were determined by heating at 120°–125°.

Water determination:

0.4724 gram substance lost 0.1214 gram H_2O.

	Calculated for $C_8H_6O_4N_2Na.4H_2O$	Found
H_2O	25.82	25.7

Nitrogen determination in the anhydrous salt (Kjeldahl):

	Calculated for $C_8H_9O_4N_2Na$	Found
N	20.29	20.31

In order to obtain the free barbiturylacetamide the above sodium salt was dissolved in a small volume of hot water and the solution acidified with hydrochloric acid and cooled. The amide separated in the form of needles and was purified by recrystallization from hot water. It melted from 258°–261° with decomposition. The amide was dried for analysis (Kjeldahl) at 100°.

	Calculated for $C_8H_7O_4N_2$	Found
N	22.7	22.44

Barbituryl-5-acetic acid, $\begin{matrix} NH—CO \\ | \quad | \\ CO \quad CHCH_2COOH \\ | \quad | \\ NH—CO \end{matrix}$.—This acid was prepared by digesting one gram of the above sodium salt with 30 cc. of 20 per cent. hydrochloric acid. After concentration of the acid solution and cooling, the acid separated as light brown, hexagonal plates. It was purified by crystallization from boiling water and separated, on cooling, in plates which charred at 230° and then decomposed at 250° with effervescence. The acid occluded moisture and was dried for analysis at 125°.

	Calculated for $C_8H_6O_5N_2$	Found
N	15.05	15.13

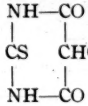
The Action of Phosphorus Oxychloride on the Sodium Salt of Barbituryl-5-acetamide.—An attempt to condense this amide to a 1,3,9-pyrimazole, by means of this halide, was unsuccessful. Four and sixty-six hundreths grams of the dry salt were suspended in 30 cc. of phosphorus oxychloride and the mixture digested for 4 hours. The phosphorus halide had assumed a dark color and suspended in the fluid was a dark brown substance, which was apparently a mixture of the unaltered amide and sodium chloride. This was separated and the phosphorus oxychloride then evaporated, when a dark oily

residue was obtained. There was not, however, sufficient material for experimental purposes and, furthermore, a nitrogen determination indicated that it was not a definite substance. The product insoluble in the phosphorus oxychloride was dissolved in hot water, decolorized by digestion with bone coal and the solution concentrated. On cooling, well defined crystals, in the form of plates, separated and decomposed at about 248°–250° with violent effervescence. This substance was very soluble in hot and difficultly soluble in cold water. It was identified as barbituryl-5-acetic acid. A mixture of the substance with some of this acid melted at 248°–250°. Nitrogen determination (Kjeldahl) after drying at 125°:

	Calculated for $C_6H_6O_5N_2$	Found
N	15.05	15.24

The Condensation of Thiourea with Triethyl Ethane-α,α,β-tricarboxylate, $C_2H_5OOCCH_2CH(COOC_2H_5)_2$

Thiobarbituryl-5-acetamide,



$.H_2O$.—Three and eight-tenths grams of sodium were dissolved in 30 cc. of absolute alcohol and 3.1 grams of thiourea dissolved in the solution. Ten grams of the carboxylate were then added and the mixture warmed on the steam bath for 4.5 hours. The alcohol was then evaporated and the residue triturated with 30 cc. of cold water. A clear liquid was obtained, which separated in two distinct layers. These were carefully separated by means of a separatory funnel and each acidified with hydrochloric acid. No precipitate deposited from the upper layer and on evaporation only sodium chloride was obtained. From the lower layer, after acidifying and cooling, 3.1 grams of the amide were obtained. It was purified by dissolving in an excess of boiling water and then concentrating to a small volume and cooling, when it separated in the form of needles. This compound charred at 252° and then decomposed with effervescence when heated to 272°. It was dried for analysis at 100°.

Sulphur determination (Carius):
0.1694 gram substance gave 0.1835 gram $BaSO_4$.
Nitrogen determination (Kjeldahl):

	Calculated for $C_8H_7O_3N_3S.H_2O$	Found
S	14.67	14.8
N	19.18	19.04

In another experiment, in which we used 3.0 grams of sodium, 5.0 grams of thiourea and 14.0 grams of the carboxylic ester, the digestion was continued for only 2.5 hours, when the excess of alcohol was evaporated and the residue dissolved in an excess of water. On acidifying with concentrated hydrochloric acid, to avoid too great dilution, and cooling we obtained 2.0 grams of a substance which was difficultly soluble in water and insoluble in alcohol. This gave, after drying at 100°, 19.62 and 19.69 per cent. of nitrogen and decomposed at about 258° with effervescence. In order to purify this product it was finally dissolved in a large volume of water and the solution then concentrated and cooled, when thiobarbituryl-5-acetamide separated in the form of needles, and decomposed at 272° with effervescence. It was dried for analysis at 105°.

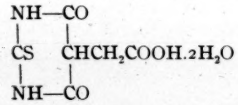
	Calculated for $C_8H_7O_3N_3S.H_2O$	Found	
		I	II
N	19.18	19.00	18.87

In a third experiment the sodium salt of thiobarbituryl-5-acetamide and thiobarbituryl-5-acetic acid were isolated as follows: The condensation was effected as described in the previous experiment and the alcohol evaporated as usual. The solid residue was then dissolved in about 13 cc. of water, the solution concentrated and finally allowed to stand for several hours. The sodium salt separated in the form of long, colorless prisms which had no definite melting point. It was very soluble in water and separated from a concentrated solution in an anhydrous condition. Analysis (Kjeldahl):

	Calculated for $C_8H_8O_3N_3SNa$	Found
N	19.00	19.4

When the aqueous solution above, after filtration from the sodium salt, was acidified strongly with hydrochloric acid a

crystalline product separated. This dissolved in hot water, but on cooling the solution two distinct crystalline forms, needles and plates, were obtained. A nitrogen determination also indicated that we were not dealing with a definite substance but apparently a mixture of thiobarbituryl-5-acetamide and the corresponding acid. In order to obtain the pure acid the mixture was finally dissolved in 50 cc. of 20 per cent. hydrochloric acid and the solution concentrated to a small volume on the steam bath. The amide underwent hydrolysis by this treatment and, on cooling, *thiobarbituryl-5-acetic acid*,



separated in the form of needles. The acid contained two molecules of water of crystallization and decomposed with effervescence when heated above 230°.

Water determination:

0.6492 gram substance lost at 105° 0.0932 gram H_2O.

	Calculated for $C_6H_6O_4N_2S.2H_2O$	Found
H_2O	15.1	14.34

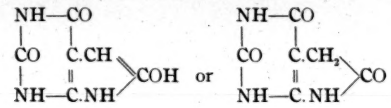
Nitrogen determination (Kjeldahl) in the anhydrous acid:

	Calculated for $C_6H_6O_4N_2S$	Found
N	13.86	13.86

The Condensation of Diethyl Cyanosuccinate, $C_2H_5OOCCH(CN)CH_2COOC_2H_5$, *with Urea*

This ester condenses normally with urea, forming a pyrimidine. The reaction, however, is not smooth and the yields of condensation products formed are small. Furthermore, it is extremely difficult to obtain consistent yields although the greatest care be taken to work under similar conditions. Secondary products are formed in small amount, which are difficult to separate. Of the several experiments which we carried out, we shall describe only two. These illustrate the nature of the reactions and the products formed.

Seven and five-tenths grams of the cyanosuccinic ester were condensed with urea (2.5 grams) by digestion in alcohol and in the presence of sodium ethylate (2.0 grams of sodium). After warming on the steam bath for about 16 hours the alcohol was then evaporated and the residue dissolved in 15 cc. of water. The fluid separated in two layers. The upper layer was acidified with hydrochloric acid and the solution concentrated but nothing but sodium chloride was obtained. The lower layer was likewise acidified with hydrochloric acid and allowed to stand, when a brownish colored powder deposited. This substance was insoluble in water, alcohol and glacial acetic acid. It dissolved in a cold, dilute sodium hydroxide solution and was reprecipitated unaltered by addition of hydrochloric acid. When heated in a capillary tube it began to darken at about 295°, but did not melt below 320°. Nitrogen determinations (Kjeldahl) agreed with the calculated value for *2,6,8-trioxy-1,3,9-pyrimazole*,



or

	Calculated for $C_8H_5O_3N_3$	Found I	Found II
N	25.15	25.5	25.16

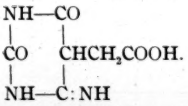
After separation of the pyrimazole, the filtrate was acidified strongly with hydrochloric acid and then concentrated on the steam bath. On cooling barbituryl-5-acetic acid separated and was purified by crystallization from hot water. It separated in plates, which melted at 248°–250° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_6H_6O_3N_2$	Found
N	15.05	15.07

The yields of the pyrimazole and the barbituryl-5-acetic acid were small.

In a second experiment 7 grams of the cyanosuccinate were condensed with 2.2 grams of urea by digestion for 5.5 hours. The alcohol was then evaporated and the residue dissolved in

20 cc. of water. This liquid formed two layers as described in the preceding experiment. These were carefully separated and acidified with hydrochloric acid. Only a small precipitate deposited from the upper layer, while from the lower layer a brown powder separated, which dissolved in hot water and deposited again on cooling. This substance did not melt below 338° and a nitrogen determination indicated that we were dealing with *4-iminobarbituryl-5-acetic acid*,



	Calculated for $C_6H_7O_4N_3$	Found
N	22.7	23.2

When the acid filtrate above was concentrated and cooled a crystalline substance separated, which was identified as barbituryl-5-acetic acid. It decomposed at 248°. A mixture of this product and some of the pure acid melted at the same temperature.

NEW HAVEN, CONN.
January 13, 1913

[Contributions from the Sheffield Laboratory of Yale University]

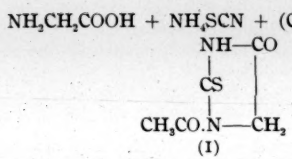
CCVI.—HYDANTOINS
THE ACTION OF AMMONIUM AND POTASSIUM THIOCYANATES ON α-AMINO ACIDS

BY TREAT B. JOHNSON AND BEN H. NICOLET

[TWENTY-FIRST PAPER]

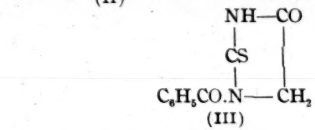
It has been shown by one of us and his coworkers[1] that α-amino acids react with a thiocyanate in an acetic anhydride solution, in an unique manner, with formation of the corresponding 3-acetylthiohydantoins (I). Every α-amino monocarboxylic acid which we have examined has reacted in this manner. The transformation may be represented as follows:

[1] Johnson and Nicolet: J. Am. Chem. Soc., **33**, 1973. Johnson: J. Biol. Chem., **11**, 97. Johnson and Guest: THIS JOURNAL, **47**, 242; **48**, 103. Johnson and O'Brien: J. Biol. Chem., **12**, 205.



(I)

It has also been shown that it is apparently a normal reaction for acyl derivatives of α-amino acids (II) also to react with thiocyanates, in the same medium, giving the corresponding acylthiohydantoins (III). The reaction with hippuric acid (II) may be represented as given below. This reaction, however, has received little attention, so far, because of pressure of other work, but it is now being investigated and will be applied to various acyclic and cyclic compounds containing the peptide grouping —NH.CH_2.CO—. The results will be published later.



(II)

(III)

During the progress of our investigation we had no reason to suspect that the nature of the inorganic thiocyanate would influence, to any extent, the course of these reactions. Komatsu[1] had previously applied the first reaction successfully with potassium thiocyanate and the two amino acids, glycocoll and alanine, but, as the writers[2] have already shown, he entirely misinterpreted the changes involved and consequently his conclusions were wrong. It was not until we found that our stock of Kahlbaum's ammonium thiocyanate was actually mislabeled potassium thiocyanate that we made the discovery[3] that these two salts do not react with the same readiness with α-amino acids under the conditions of our experiments. A

[1] Mem. Coll. Sci. Eng., Kyoto Univ. (Japan), **3**, 1 (1911).

[2] *Loc. cit.*

[3] Johnson: THIS JOURNAL, **49**, 68.

repetition of our work now reveals the fact that both salts combine with amino acids with formation of the same thiohydantoins, but, on the other hand, we find that the best yields, in every case so far examined, are obtained when the reactions are applied with ammonium thiocyanate.

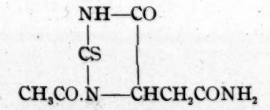
At present we shall not attempt to offer an explanation for this remarkable difference in the behavior of these two thiocyanates towards α-amino acids. Efforts will be made to obtain new data wh ch will enable us to draw more definite conclusions as to the mechanism of these changes. Furthermore, it is not improbable that, by the proper change of experimental conditions, thiohydantoins may be formed as well from potassium thiocyanate as by using the ammonium salt.

In the experimental part of this paper a description is given of the behavior of these two thiocyanates towards phenylalanine, asparagine, tyrosine, hippuric acid, alanine and pyrrolidonecarboxylic acid.

EXPERIMENTAL PART

In this investigation of the action of ammonium and potassium thiocyanates on α-amino acids the following proportions, unless otherwise stated, were always used, viz., two grams of the amino acid and 1.5–2.0 grams of the thiocyanate suspended in a mixture of 9 cc. of acetic anhydride and 1 cc. of acetic acid. These mixtures were then heated for 20 minutes on a steam bath, when, in every case, a clear solution was obtained. This was then poured into about 50 cc. of cold water in order to precipitate the acylhydantoin and the latter purified by recrystallization from alcohol or water.

The Conversion of Asparagine into 2-Thio-3-acetylhydantoin-4-acetamide[1]



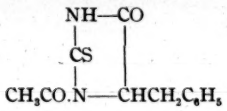
With Ammonium Thiocyanate.—With this reagent the formation of the acylthiohydantoin is very smooth. The liquid

[1] Johnson and Guest: THIS JOURNAL, **48**, 103. Johnson: *Loc. cit.*

assumes, on warming, a light yellow color and on pouring into water the thiohydantoin separates immediately as a yellow, crystalline substance. The crude hydantoin melted at 220° and the yield was 1.65 grams, or about 50 per cent. of the theoretical. The purified hydantoin melted at 223–224°.

With Potassium Thiocyanate.—The acetic anhydride solution of the amino acid amide was not colored strongly by heating with this salt and apparently there was little decomposition. The reaction, however, was not smooth. On pouring the liquid into water a clear yellow solution was obtained and no thiohydantoin separated after standing for 15 hours. After 24 hours about 0.2 gram of the hydantoin had separated, corresponding to a yield of about 6 per cent. The results were the same whether we used Kahlbaum's or Merck's potassium thiocyanate.

The Conversion of Phenylalanine into 2-Thio-3-acetyl-4-benzylhydantoin[1]



With Ammonium Thiocyanate.—The acylthiohydantoin is formed smoothly by the action of this salt on the amino acid. The acetic anhydride solution assumes a light yellow color on warming, and on pouring into water the hydantoin separates as an oil, which soon crystallizes. The yield of crude hydantoin is generally about 2.8 grams, or 94 per cent. of the theoretical.

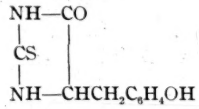
With Potassium Thiocyanate.—When this salt was employed an oil was obtained by pouring into cold water, which partially solidified after standing 15 hours. The yield of crude material was 2.2 grams. This hydantoin was purified by crystallization from boiling alcohol and separated, on cooling, in colorless prisms or hexagonal plates. The compound melts at 170° to a clear oil instead of 257° as erroneously given in our previous paper.[2] The hydantoin is difficultly soluble in water and is

[1] Johnson and O'Brien: J. Biol. Chem., **12**, 205. Johnson: *Loc. cit.*

[2] Johnson and O'Brien: *Loc. cit.*

transformed quantitatively by hydrolysis with hydrochloric acid into the thiohydantoin of phenylalanine melting at 185°.

The Conversion of Tyrosine into 2-Thio-4-(p-hydroxybenzyl)-hydantoin



With Ammonium Thiocyanate.—In this experiment 2.0 grams of Kahlbaum's active tyrosine and 2.0 grams of the thiocyanate were suspended in a mixture of 30 cc. of acetic anhydride and 1 cc. of glacial acetic acid and the mixture then heated on the steam bath until a clear solution was obtained. On cooling, nothing separated and on pouring into cold water an oil deposited, which dissolved again on warming gently. The clear aqueous solution was then evaporated, when we obtained apparently the acylthiohydantoin as a viscous oil, which was extremely soluble in water and showed no signs of crystallizing after long standing. The crude product was dissolved in hydrochloric acid and the solution evaporated on the steam bath, when we obtained the tyrosinethiohydantoin in a crystalline condition. The yield was 2.0 grams, or 82 per cent. of the theoretical. This thiohydantoin is soluble in about 10 parts of hot water, and separates from this solvent, on cooling, in yellow needles melting at 211° without apparent decomposition. After repeated recrystallizations the compound can be obtained nearly colorless. It is readily soluble in 95 per cent. alcohol.

Analysis (Kjeldahl):

	Calculated for $C_{10}H_{10}O_2N_2S$	Found
N	12.60	12.41

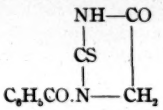
The thiohydantoin is soluble in 5 per cent. potassium hydroxide solution, and on acidifying the solution it is recovered unaltered and melting at 211°.

With Potassium Thiocyanate.—We used in this experiment 1 gram of tyrosine, 0.7 gram of potassium thiocyanate, 10 cc.

of acetic anhydride and 0.7 cc. of glacial acetic acid. Otherwise the procedure was the same as described in the previous experiment. The anhydride solution assumed no red color during the heating and there was no evidence of decomposition, but after pouring into water and subjecting to hydrolysis with hydrochloric acid, we obtained only 0.2 gram of tyrosine-thiohydantoin. Therefore, in this case also the best results are obtained when the reagent used is ammonium thiocyanate.

Desulphurization of Tyrosinethiohydantoin.—Seventy-five hundredths gram of the thiohydantoin was desulphurized by boiling for 1.5 hours with a solution of 4 grams of chloroacetic acid in 5 cc. of water. On cooling, 0.6 gram of the hydantoin of tyrosine separated and melted at 262° with slight effervescence.[1]

The Formation of 2-Thio-3-benzoylhydantoin from Hippuric Acid[2]



This thiohydantoin is formed by the action of either ammonium thiocyanate or potassium thiocyanate on hippuric acid in acetic anhydride solution. The yields of hydantoin obtained are, however, decidedly different. In the case of the ammonium salt the reaction is very smooth and the yield of hydantoin generally averages about 85–88 per cent. of the theoretical. In fact, the thiohydantoin separates almost immediately in a crystalline condition after pouring the anhydride solution into cold water and is nearly pure after one recrystallization from alcohol. On the other hand, by using the potassium salt the formation of the thiohydantoin is far less smooth and we have never succeeded in obtaining a yield of this compound greater than 50 per cent. of the calculated amount. We have used different specimens of potassium thiocyanate and acetic anhydride, but, in every case when we

[1] Wheeler and Hoffman: THIS JOURNAL, **45**, 368.
[2] Johnson and Nicolet: *Loc. cit.*

used this salt, the anhydride solution always assumed a deep red color within a few minutes and if heated longer than 30 minutes it generally became opaque. On pouring into water, after the reaction was complete, the thiohydantoin generally is obtained very impure and separates as a dark, heavy oil, which crystallizes only after long standing. The purity of the hydantoin is also influenced by the length of time of heating. We find that the reaction proceeds slowly at ordinary temperature (20°–30°), but even when conducted under these conditions the yield is only about 50 per cent. of that obtained by using ammonium thiocyanate. In order, therefore, to prepare this thiohydantoin in quantity from hippuric acid it is necessary to use ammonium thiocyanate and the following procedure is recommended for its separation: Suspend 2.0 grams of hippuric acid (pulverized) and 1.25 molecular proportions of dry ammonium thiocyanate in a mixture of 9 cc. of acetic anhydride and 1 cc. of glacial acetic acid and connect the flask with a return condenser. Then heat on the steam bath at 90°–100° until the hippuric acid and ammonium salt completely dissolve and the solution assumes an orange color. This requires about 20 minutes' heating. The anhydride solution is then cooled and poured into about 5 parts of cold water and the mixture stirred, when the hydantoin will generally crystallize immediately. This product is very pure, has a light yellow color and needs no further purification before conversion into the 2-thiohydantoin, $NH.CS.\underset{\llcorner\!\!\!

hydantoin is very smooth, when this thiocyanate is used, and the yield is excellent. The hydantoin separates immediately on pouring the acetic anhydride solution into water and generally melts without further purification at 166° to an oil.

With Potassium Thiocyanate.—When this salt is used there is no apparent indication that the reaction is abnormal while heating the anhydride solution at 90°–100°. The thiocyanate dissolves completely and the liquid assumes no color. The hydantoin, however, is not obtained in good yield. On pouring the anhydride solution into cold water the hydantoin first separates as a heavy oil, which finally solidifies. The weight of the crude product was only 1.3 grams, or about 34 per cent. of the theoretical.

The Action of Thiocyanates on Pyrrolidonecarboxylic Acid

Any derivative of this cyclic acid which is characteristic and suitable for its identification is of interest because of the probability that pyrrolidonecarboxylic acid is one of the constituents of protein.[1] A derivative of this character is the corresponding thiohydantoin, which has been described in a previous paper from this laboratory.[2] It is formed by the action of ammonium thiocyanate on this acid and also, but in small amount only, by the action of the potassium salt. If the potassium salt is used and the experiment is conducted under the conditions outlined in the introduction to the experimental part of this paper a product is formed which is very impure and enough of the hydantoin cannot be obtained for experimental purposes. On the other hand, with ammonium thiocyanate the product is crystalline and there is no difficultly in obtaining good yields. This hydantoin crystallizes from water or alcohol in prismatic crystals which melt at 206°.

NEW HAVEN, CONN.
January 13, 1913

[1] Abderhalden and Wurm: Z. physiol. Chem., **32**, 160.
[2] Johnson and Guest: *Loc. cit.*

CONCERNING POTASSIUM β-FERRICYANIDE

By H. L. Wells

Hauser and Biesalski[1] have recently attempted to show that the isomeric form of potassium ferricyanide described by Locke and Edwards[2] is merely the ordinary salt contaminated with a little colloidal Prussian blue.

Since the investigation of Locke and Edwards was made in this laboratory, and since these gentlemen are no longer engaged in chemical research, I am taking occasion to show that Hauser and Biesalski are entirely mistaken in regard to this matter.

Hauser and Biesalski appear to assume that the only differences between the α- and β-ferricyanides in their reactions with the salts of the heavy metals are slight variations in the colors of the precipitates. This is absolutely incorrect, as they ignore several important reactions, particularly the one with a dilute nitric acid solution of bismuth nitrate, which was mentioned repeatedly and very prominently in the articles of Locke and Edwards, and was used by them as the principal means of testing the purity of their preparations of β-ferricyanide.

I have found one of the original preparations of potassium β-ferricyanide, made by Locke and Edwards, which has been kept here for about 13 years. It still gives a practically clear solution with water, and the solution gives no precipitate with bismuth nitrate, while ordinary potassium ferricyanide gives an immediate precipitate, even in very dilute solutions.

This reaction alone is sufficient to show that Hauser and Biesalski are absolutely wrong in their conclusions, for it is inconceivable that the presence of a minute amount of colloidal Prussian blue should prevent the formation of an exceedingly slightly soluble precipitate, and, moreover, Locke and Edwards found this reaction to furnish a delicate test for the ordinary ferricyanide in the presence of large amounts of the isomer.

It is to be noticed also that Hauser and Biesalski make no mention of the fact that Locke and Edwards found the β-ferri-

[1] Ber. d. chem. Ges., **45**, 3516 (1912).

[2] This Journal, **21**, 193, 413.

cyanide to contain a molecule of water of crystallization. They assume that the presence of a trace of Prussian blue is capable of modifying the habit of the crystals, but it is impossible to imagine that this minute quantity of colloidal substance, which they estimate as amounting to "0.001 Mole auf 1 Mol Ferricyankalium," should be capable of causing the addition of water of crystallization to the main substance.

The recent important work of Bellucci and Sabatini,[1] who have shown that the α- and β-ferricyanides are nitrile and isonitrile forms, is mentioned by Hauser and Biesalski as furnishing the only chemical evidence of the existence of two different modifications of potassium ferricyanide. This is not true, since Locke and Edwards found numerous chemical distinctions, among which are the bismuth reaction and the difference in water of crystallization, which have already been discussed.

It appears, however, that Hauser and Biesalski have confirmed the results of Bellucci and Sabatini as well as could be expected in view of the apparent circumstance that, in being ignorant of the bismuth test, they were not in a position to prepare pure potassium β-ferricyanide. They admit that the formation of ferric imido ester proceeds more smoothly with ordinary potassium ferricyanide than with the form "contaminated with Prussian blue," although they think that this difference is due to a catalytic action of the impurity. Their statement that the ester may be produced, although in much smaller quantity, from the "second form" of the ferricyanide is not worthy of serious consideration, since it appears that they knew no method of testing the β-ferricyanide for the original salt, which, as Locke and Edwards have shown, is an impurity that is avoided with difficulty.

There seems to be no excuse for the evident ignorance on the part of Hauser and Biesalski of important features in the work of Locke and Edwards, for they refer to the original articles, and, since they are situated at the University of Berlin, these articles were certainly easily accessible to them.

SHEFFIELD LABORATORY, NEW HAVEN, CONN.
January, 1913

[1] Atti accad. Lincei, **22**, I, 176.

A STUDY OF THE CONDUCTIVITY, DISSOCIATION AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY OF CERTAIN INORGANIC SALTS IN AQUEOUS SOLUTION, AS CONDITIONED BY TEMPERATURE, DILUTION, HYDRATION AND HYDROLYSIS

By E. J. Shaeffer and Harry C. Jones

The work described in this paper is but a part of the systematic study of the conductivity, dissociation and temperature coefficients of conductivity of electrolytes which was begun in this laboratory twelve years ago in connection with the solvate theory of solution proposed by Jones.[1] We have studied, in this investigation, inorganic salts by the modified Kohlrausch conductivity method, and in interpreting the results we shall make use of what is known regarding the nature of solution. The theory of electrolytic dissociation,[2] the solvate theory of Jones,[3] the relation pointed out by Dutoit and Aston,[4] connecting the association of a solvent with its dissociating power, and the Thomson[5]-Nernst[6] hypothesis bringing out the relations between dissociating power and dielectric constant of the solvent, enable us to explain satisfactorily a very large part of the conductivity data obtained in this investigation.

HISTORICAL REVIEW

Jones and his coworkers,[7] in discussing conductivity measurements, have given satisfactory reviews of the conductivity work done previous to that carried out in this laboratory. In this review only the work bearing on the conductivity of inorganic compounds in aqueous solutions will be considered. The systematic study of the nature of inorganic salts in aqueous solution and their dissociation as measured by the modified

[1] This Journal, **23**, 89 (1900).
[2] Z. physik. Chem., **1**, 631 (1886).
[3] This Journal, **23**, 103 (1900).
[4] Compt. rend., **128**, 540 (1899).
[5] Phil. Mag., **36**, 320 (1894).
[6] Z. physik. Chem., **13**, 531 (1894).
[7] This Journal, **34**, 358 (1905); **40**, 355 (1908); **46**, 240 (1911); **48**, 500 (1912).

Kohlrausch conductivity method was begun by Jones and West in 1904.

It was known that conductivity increased with dilution and rise in temperature, and that the dissociation of electrolytes at high temperatures decreased with rise in temperature, but not much of a reliable nature was known regarding the change in dissociation of electrolytes over the lower temperature ranges with rise in temperature. It was also known that dissociation increased with increase in dilution up to a certain point, where it was complete. For salts, temperature coefficients of conductivity were shown to increase with rise in temperature, while for acids but little change with rise in temperature manifested itself. Satisfactory explanations for most of these facts were lacking. Moreover, the literature contained but a small amount of reliable data regarding the dissociation of important inorganic acids and salts over wide ranges of temperature and dilution. One of the objects in undertaking the investigation was to supply these important data.

Confidence in conductivity methods was greatly strengthened by the work of Jones and West.[1] They did much to improve the accuracy of conductivity measurements. Dissociation over a range of temperature from 0°–35° was found to decrease with rise in temperature. This they pointed out was in accordance with the relation of Dutoit and Aston,[2] connecting the association of a solvent with the dissociation of the dissolved substance. Ramsay and Shields[3] had already pointed out that the association of a solvent decreased with rise in temperature. This result was in accord with the work of von Willer[4] and the Thomson[5]-Nernst[6] hypothesis, which showed that the dissociating power of a solvent increased with its dielectric constant, and that the effect of rise in temperature was to decrease the dielectric constant of the solvent. They found that the percentage temperature coefficients of conductivity

[1] THIS JOURNAL, **34,** 357 (1905).
[2] Compt. rend., **125,** 240 (1897).
[3] Z. physik. Chem., **12,** 433 (1893).
[4] Phil. Mag., [6] **7,** 655 (1904).
[5] *Ibid.*, **38,** 320 (1894).
[6] Z. physik. Chem., **13,** 531 (1894).

decreased with rise in temperature, and that the temperature coefficients of conductivity, in the case of salts, increased with rise in temperature, while for acids they decreased.

The work of Jones and his coworkers had already proved that a large number of compounds were hydrated in aqueous solutions, and in Monograph No. 60 of the Publications of the Carnegie Institution of Washington are recorded the approximate compositions of a large number of hydrates. With these conceptions in mind, Jones[1] pointed out a number of relations between conductivity, temperature coefficients of conductivity and the present hydrate theory. Since most ions are hydrated in aqueous solutions, with rise in temperature these unstable hydrates would break down. The effect would be to decrease the mass of the ion, and since the viscosity of the solutions studied changed but slightly with rise in temperature, and the driving power of the current was but little increased, the decreasing mass of the ion is the chief factor in conditioning the increase in conductivity with rise in temperature. It was pointed out that, due to the greater complexity of the hydrates at higher dilutions, we should expect them to change more at high than at low dilutions with rise in temperature. This explains the fact that temperature coefficients of conductivity are greater at high than at low dilutions, and also why the increase in the value of the coefficient is greatest for those substances that have the greatest hydrating power. Jones and Pearce[2] called attention to the fact that the hydrating power of a salt is primarily a function of the cation, and that its ability to hydrate is an inverse function of its atomic volume. Before this relation was pointed out, it was difficult to see how the potassium, rubidium and caesium ions with large atomic volumes could have larger migration velocities than the sodium ions of smaller mass and atomic volume.

Jones and Jacobson[3] continued the work of West. They improved earlier methods and obtained results which substantiated those noted by Jones and West. The effect of

[1] THIS JOURNAL, **35**, 445 (1906).
[2] *Ibid.*, **38**, 736 (1907).
[3] *Ibid.*, **40**, 355 (1908).

hydrolysis, acting so as to vitiate the true value of $\mu\infty$, was mentioned. They, furthermore, concluded that salts which are strongly hydrated in solution show a greater increase in conductivity with rise in temperature than salts which are slightly hydrated.

Having these facts in mind, Clover and Jones[1] continued the study of the problem, working at temperatures ranging from 35°–80°. They made it possible to determine conductivities to a temperature as high as 65°. Certain difficulties, such as the solubility of glass and changes in the cell constants, were overcome. They concluded that it is not practical to measure the conductivity of a solution at 80° unless its concentration is around 0.01 N. The relations pointed out at lower temperatures were also found to hold at higher temperatures. From these results and previous ones, it was now clearly seen that substances with equal hydrating power have approximately the same temperature coefficients of conductivity. As conductivity depends largely on the complexity of the hydrate formed by the ions, we should expect this to be true from the hydrate theory. The sulphates were excepted from the above conclusion, because they are largely polymerized in aqueous solutions. At these temperatures, it was found that dissociation decreased slightly with rise in temperature.

West and Jones[2] continued the work at these high temperatures. They improved still further the methods of measuring conductivity at high temperatures, and obtained results very similar to those found by Clover and Jones.

Hosford and Jones[3] worked at temperatures ranging from 0°–65°. The effect of hydrolysis as causing abnormally great conductivity was pointed out, and it was stated that hydrolysis increases both with dilution and rise in temperature. The effect of hydrolysis on the green variety of chromic salts was shown to be less than on the violet form when the dilution increases. It was suggested that the abnormally rapid increase in conductivity is often caused by a decrease in polymerization. The con-

[1] THIS JOURNAL, **43**, 508 (1910).
[2] *Ibid.*, **44**, 508 (1910).
[3] *Ibid.*, **46**, 240 (1911).

ductivity of double salts at temperatures ranging from 0°–65° was found to be less than the sum of the conductivities of the constituent salts, as had been pointed out by Jones and his coworkers[1] at 25°.

Miss Winston and Jones[2] extended the work already done at low temperatures, and their results confirmed those earlier obtained. To account for the increase in percentage dissociation of certain salts with rise in temperature, and large temperature coefficients where there is no reason to expect large hydration, the view that inductive action takes place through the solvent between charged ions and neutral molecules, giving rise to complex ions and molecules in solutions, was advanced by Miss Winston.[2]

The investigation of Howard and Jones[3] continued the work done at higher temperatures. A time factor of hydrolysis was noted, and its effect on conductivity measurements pointed out. This review brings the work up to the present.

Since the beginning of this work, complete conductivity data for 110 of the more common inorganic compounds have been carefully worked out over wide ranges of dilution and temperature. The work has also been extended to about 90 of the more common organic acids. A good idea of the scope of this work may be obtained from a recent publication by Jones[4] and his coworkers in which all the best data obtained thus far have been tabulated and discussed.

PURPOSE OF THIS INVESTIGATION

The object in carrying out this work was to accumulate more data in regard to the dissociation of electrolytes over wide ranges of temperature and dilution, to improve and study the well known Kohlrausch conductivity method as a means of measuring dissociation, to test more fully the conclusions already reached by investigators in this laboratory and to discover new relations from the data obtained.

[1] THIS JOURNAL, **19**, 83 (1897); **22**, 5 (1899); **23**, 110 (1899); **25**, 349 (1901).
[2] *Ibid.*, **46**, 368 (1911).
[3] *Ibid.*, **48**, 500 (1912).
[4] Carnegie Institution of Washington, Publication No. **170**.

EXPERIMENTAL DISCUSSION

Apparatus

The Bridge.—About half of the conductivity readings for the lower temperature work were taken from a straight slide wire Wheatstone bridge, calibrated by the method of Strouhal and Barus.[1] The remainder of the work at lower temperatures and all of the work at higher temperatures was done with an improved circular slide wire bridge, made by Leeds and Northrup. By means of this bridge, it was possible to read the resistance of the solution down to fractions of a millimeter.

Rheostat.—The resistance box was standardized against a rheostat which, in turn, had been standardized by the Bureau of Standards in Washington. Considerable stress should be laid upon the necessity of keeping all connections absolutely clean, especially the plugs of the rheostat. The usual methods of cleaning the connections are far from sufficient.

It was found that unless the wires connecting the cells and rheostat were short and of a large diameter, very appreciable errors were introduced in measuring the resistances of concentrated solutions.

Cells.—The cells were of the general types which have been in use in this laboratory for some time. They have recently been described and sketched.[2] As a rule, eight dilutions of each salt were studied, and for each dilution there was a cell the distance between whose electrodes was so arranged that clear minima could be obtained on the bridge. The nine cells had done long service at both high and low temperatures, and from tests it was concluded that practically all soluble matter had been removed from them when heated to temperatures as high as 65°.

During the course of this investigation thirty-five inorganic salts were studied, and the cell constants were taken twenty-three times. No difficulty at all was experienced in keeping the electrode distance of the cells constant for the temperature range 0°–35°. Clover and Jones[3] and West and Jones[4]

[1] Wied. Ann., **10,** 32 (1880).
[2] Carnegie Institution of Washington, Publication No. **170,** p. 5.
[3] THIS JOURNAL, **43,** 195 (1910).
[4] *Ibid.*, **44,** 511 (1910).

experienced difficulty in keeping the electrode distance of the cells constant for the temperature range 35°–65°. Their recommendations were carefully adhered to. At the very beginning of the work at high temperatures, the cell constants were found to undergo change. It was caused, in our opinion, by forcing the ground glass stoppers too tightly into the cell cups. At 50° and 65°, the accumulated pressure would at times force the stoppers out of the cells, and invariably the electrode distance was disturbed. This was easily overcome by loosely stoppering the cells, and the work done at this period was repeated.

The cell constants were always determined at 25°. To determine the constants of the four cells with the greatest electrode distance, a 0.02 N potassium chloride solution was used. Its conductivity was taken as 129.7. To determine the constants of the remaining four cells, a 0.002 N solution of potassium chloride was used. Its conductivity value was determined several times and always found to be close to 135.5 For the water cell a 0.001 N potassium chloride solution was used. Its conductivity was usually close to 140.

Baths.—The baths used to maintain constant temperature were of the type described by Jones.[1] For the higher temperature work, an efficient cover was devised[2] which served to keep the temperature of the air above the cells at about the same temperature as the water surrounding the cells. During conductivity measurements the water contained in the bath was actively stirred by means of a hot air engine. The thermometers were carefully calibrated against standard ones. During part of the work, the temperature of the baths was regulated by means of thermoregulators similar to the type devised by Reid.[3] For the most part, however, the temperatures were regulated by hand.

Containing Vessels.—All flasks and burettes were calibrated and recalibrated by the method of Morse and Blalock.[4] In addition, the 1000 cc. and 500 cc. flasks used to measure

[1] Carnegie Institution of Washington, Publication No. **170**, p. 9.
[2] This Journal, **48**, 504 (1912).
[3] *Ibid.*, **41**, 148 (1909).
[4] *Ibid.*, **16**, 479 (1894).

the volume of the mother solution were calibrated also by the weight method, and very close agreements with the method of Morse and Blalock were obtained. For the higher temperature work, all containing vessels were of Jena glass. How slightly soluble this glass is will be brought out in a later connection. The 500 cc. flask used for this work was calibrated so that when it was filled to the proper mark at 20° it would contain 500 cc. of solution at 50°.[1]

Preparation of Solutions.—Whenever a salt was used at both high and low temperatures, two sets of solutions were prepared. The conductivities of both sets were determined at 35°, and thus a check upon our work was obtained. The solutions used for the lower temperature work were made up at 20°.

Since the volume changes of a solution are so great with change in temperature, we are obviously at a great disadvantage in making up solutions at temperatures very far removed from that of the room. At high temperatures, it is a well known fact that the solubility of the glass is another factor which must be taken into account. Methods described by West and Jones[2] and by Springer and Jones[3] made it possible to prepare solutions at 20° and to use these solutions for conductivity determinations at 35°, 50° and 65°.

For the high temperature work, the solutions were made up from a mother solution contained in a specially calibrated 500 cc. flask. This flask had two marks. To determine the position of the lower mark the weight of 500 cc. of distilled water at 50°, air displacement being taken into account, was used. When this flask was filled with a solution up to the mark at 20° and then warmed to 50° we had just 500 cc. at 50°. To test the correctness of the above mark, the flask was calibrated by the method of Morse and Blalock so as to contain 500 cc. at 50°. Of course, the proper corrections for these calibrations were taken into account. When a solution at 20° was added to the flask up to the 20° mark and heated to 50°, it was found

[1] THIS JOURNAL, **48**, 417 (1912).
[2] *Ibid.*, **44**, 508 (1910).
[3] *Ibid.*, **48**, 416 (1912).

that its meniscus corresponded with the calibration mark at 50° determined by the method of Morse and Blalock. With but very few exceptions, the coefficients of expansion of our most concentrated solutions were only slightly different from that of distilled water. We were thus assured that our solutions, made up at 20°, would be of the proper concentration when heated to 50°. To correct for the increase in concentration due to cooling such a solution down from 50° to 35°, the factor 0.994, as worked out by Jones and Clover,[1] was multiplied into all conductivity values obtained at 35°. The factor 1.0076,[2] when multiplied into the conductivities obtained at 65°, corrected for the decrease in concentration due to warming the solutions from 50° to 65°.

Purification of Salts.—Nearly every salt worked with in this investigation came from Kahlbaum. Just how each salt was purified and the concentration of the mother solution determined is stated above the conductivity tables for that particular salt. It is desirable to do this in some detail, since conductivity data obtained by different investigators for the same substance are often discordant, and unless the investigator makes known the method of purification, and the way in which the concentration of the mother solution was ascertained, it is difficult to tell which values are more likely to be correct. Such information is certainly of great assistance to other investigators in this field.

Conductivity Water.—All the water used in this work was purified by the method of Jones and Mackay.[3] The water thus obtained had an average conductivity of 0.7×10^{-6} at 0°.

The conductivity data are expressed in Siemens units according to well known methods of calculation.[4] Each conductivity value recorded is the average of three readings.

Ammonium Hydrogen Sulphate

The above salt was recrystallized from conductivity water. The exact strength of the mother solution was determined

[1] THIS JOURNAL, **43**, 187 (1910).
[2] *Ibid.*, **44**, 510 (1910).
[3] *Ibid.*, **19**, 91 (1897).
[4] Carnegie Institution of Washington, Publication No. **170**, p. 11.

by precipitation of the sulphuric acid by means of barium chloride.

Table I.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	207.2	35.9	223.8	31.4	235.3	27.5
8	263.5	45.6	286.0	40.1	303.2	35.5
32	339.2	58.8	374.2	52.5	396.5	46.4
128	433.9	75.2	485.9	68.2	525.3	61.4
512	510.2	88.4	593.5	83.3	666.1	77.9
1024	543.9	94.2	647.1	90.8	794.5	93.0
2048	560.0	97.0	681.5	95.6	820.6	96.0
4096	577.2	100.0	712.5	100.0	855.2	100.0

Table II.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	1.11	0.54	0.77	0.34
8	1.50	0.57	1.15	0.40
32	2.33	0.69	1.49	0.40
128	3.47	0.80	2.63	0.54
512	5.55	1.08	4.84	0.82
1024	6.88	1.26	9.83	1.52
2048	8.10	1.25	9.27	1.36
4096	9.02	1.56	8.85	1.23

Tetraethylammonium Iodide

The mother solution was standardized by weighing the dry and purified salt.

Table III.—Conductivity

V	0°	12°.5	25°	35°
8	38.6	54.6	72.8	88.5
32	46.5	65.4	86.8	105.0
128	51.1	72.1	95.4	114.8
512	52.8	73.9	98.0	118.4
1024	53.3	75.2	99.3	119.7
2048	54.4	77.0	101.7	122.5
4096	54.0	76.5	101.6	122.9

Table IV.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.28	3.31	1.46	2.67	1.57	2.15
32	1.51	3.25	1.70	2.60	1.82	2.09
128	1.67	3.29	1.86	2.56	1.94	2.03
512	1.69	3.20	1.92	2.59	2.04	2.08
1024	1.76	3.20	1.93	2.58	2.04	2.07
2048	1.78	3.27	1.98	2.57	2.08	2.04
4096	1.80	3.32	2.00	2.61	2.12	2.08

Table V.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	70.9	70.9	71.6	72.0
32	85.5	84.9	85.3	85.4
128	93.1	93.6	93.7	93.4
512	97.1	95.9	96.3	96.3
1024	98.0	97.7	97.6	97.5
2048	100.0	100.0	100.0	99.7
4096	99.2	99.4	99.9	100.0

Ammonium Sodium Hydrogen Phosphate

It was found that concentrated solutions of this salt decomposed at about 25°. For that reason it could not be safely purified by ordinary methods. The phosphoric acid in the mother solution was determined by means of magnesia mixture.

Table VI.—Conductivity

V	0°	12°.5	25°	35°
8	65.6	...	....	...
32	84.4	119.2	158.7	186.5
128	96.5	136.7	181.4	216.6
512	100.7	141.4	186.4	221.6
1024	104.7	145.7	193.6	235.2
2048	103.9	144.7	190.9	229.2

Table VII.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	2.78	3.30	3.16	2.65	2.78	1.49
128	3.21	3.32	3.57	2.61	3.52	1.62
512	3.26	3.24	3.60	2.54	3.52	1.58
1024	3.36	3.22	3.83	2.62	4.16	1.76
2048	3.36	3.22	3.70	2.55	3.83	1.67

Table VIII.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	62.6	...	...	...
32	80.6	81.7	81.9	79.3
128	91.3	93.1	93.7	92.1
512	96.3	97.0	96.2	94.2
1024	100.0	100.0	100.0	100.0
2048	99.2	99.3	98.6	97.4

Sodium Chloride

This salt was twice recrystallized from concentrated solutions by the addition of purified hydrochloric acid gas. It was then dried in an air bath for six hours at about 260°.

Table IX.—Conductivity

V	0°	12°.5	25°	35°
2	48.1	66.4	86.5	104.2
8	53.5	74.7	98.5	118.5
32	57.5	80.6	106.8	129.5
128	60.4	84.9	112.6	136.3
512	62.3	87.8	116.4	141.2
1024	61.6	86.9	115.4	140.0

Table X.—Temperature Coefficients

	0–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.46	3.04	1.61	2.44	1.77	2.05
8	1.70	3.19	1.90	2.54	2.00	2.03
32	1.85	3.21	2.09	2.59	2.27	2.12
128	1.96	3.24	2.21	2.60	2.37	2.11
512	2.04	3.27	2.29	2.61	2.48	2.13
1024	2.02	3.28	2.28	2.62	2.46	2.13

Table XI.—Percentage Dissociation

V	0°	12°.5	25°	35°
2	77.2	75.6	74.4	73.8
8	85.9	85.1	84.6	83.9
32	92.3	91.8	91.7	91.6
128	96.9	96.7	96.6	96.5
512	100.0	100.0	100.0	100.0
1024	98.9	99.0	99.1	99.1

Sodium Chlorate

The purified salt was dried in an air bath for two hours at 110°.

Table XII.—Conductivity

V	0°	12°.5	25°	35°
2	41.6	57.5	74.7	90.0
8	47.4	66.1	86.7	104.4
32	51.7	72.4	95.0	115.2
128	54.7	76.9	101.1	122.5
512	56.0	78.9	104.6	127.0
1024	56.2	79.0	104.1	126.3
2048	56.1	78.8	104.1	125.8

Table XIII.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	1.27	3.05	1.38	2.40	1.53	2.04
8	1.50	3.12	1.66	2.41	1.77	2.05
32	1.66	3.21	1.80	2.49	2.02	2.12
128	1.78	3.25	1.94	2.53	2.14	2.12
512	1.83	3.26	2.05	2.64	2.36	2.25
1024	1.82	3.24	2.01	2.54	2.22	2.13
2048	1.81	3.22	2.02	2.56	2.17	2.09

Table XIV.—Percentage Dissociation

V	0°	12°.5	25°	35°
2	74.0	72.8	71.4	70.8
8	84.3	83.6	82.9	81.4
32	91.9	91.6	90.8	90.7
128	97.3	97.3	96.6	96.4
512	99.6	99.8	100.0	100.0
1024	100.0	100.0	99.5	99.5
2048	99.7	99.7	99.5	99.0

Sodium Chlorate

The purified salt was dried in an air bath for two hours at 110.°

Table XV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	103.7	79.5	132.1	78.5	164.4	77.7
32	118.0	90.4	151.6	90.0	186.3	88.1
128	122.9	94.2	158.4	94.1	198.7	94.0
312	126.1	96.6	165.2	98.1	204.4	96.7
1024	130.2	99.8	167.8	99.6	211.3	100.0
2048	130.5	100.0	168.3	100.0	209.1	99.0

Table XVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.90	1.89	2.15	1.62
32	2.24	1.94	2.31	1.52
128	2.39	1.94	2.68	1.69
512	2.54	2.00	2.61	1.58
1024	2.51	1.93	2.90	1.78
2048	2.52	1.93	2.72	1.62

Sodium Perchlorate

After being recrystallized, the purified product was dried to constant weight in a weighing tube at 140°. The weighing tube was used because the salt was found to be somewhat deliquescent.

Table XVII.—Conductivity

V	0°	12°.5	25°	35°
8	49.5	69.0	90.3	109.1
32	53.5	74.9	98.5	119.2
128	56.3	78.9	104.2	126.1
512	57.0	80.0	105.7	128.8
1024	59.6	83.6	109.2	132.6
2048	60.01	84.4	111.5	135.4
4096	60.05	85.9	114.3	139.1

Table XVIII.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.56	3.15	1.70	2.46	1.88	2.08
32	1.71	3.18	1.88	2.51	2.07	2.10
128	1.81	3.21	2.02	2.56	2.19	2.10
512	1.83	3.21	2.05	2.56	2.31	2.18
1024	1.92	3.24	2.05	2.45	2.34	2.14
2048	1.95	3.25	2.17	2.57	2.39	2.14
4096	2.07	3.44	2.27	2.65	2.48	2.17

Table XIX.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	82.4	80.3	79.0	78.4
32	89.1	87.2	86.2	85.7
128	93.7	91.8	91.1	90.7
512	98.6	95.2	94.4	92.6
1024	99.2	97.3	95.5	95.3
2048	99.9	98.2	97.5	97.4
4096	100.0	100.0	100.0	100.0

Sodium Perchlorate

The mother solution for this series was prepared in exactly the same way as that for the series at lower temperatures. The specimen of salt used was not the same as that used for the lower temperature work.

Table XX.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	109.3	80.9	139.6	80.2	171.5	79.9
32	119.1	88.2	152.4	87.6	187.6	87.4
128	125.5	93.0	160.7	92.4	198.4	92.4
512	129.5	95.9	166.7	95.8	205.9	95.9
1024	132.0	97.8	170.4	97.9	211.3	98.4
2048	133.8	99.1	170.6	98.0	212.5	99.0
4096	135.0	100.0	173.9	100.0	214.6	100.0

Table XXI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.02	1.85	2.13	1.53
32	2.22	1.86	2.35	1.54
128	2.35	1.87	2.51	1.59
512	2.48	1.91	2.61	1.57
1024	2.56	1.94	2.73	1.60
2048	2.45	1.83	2.79	1.63
4096	2.59	1.92	2.71	1.56

Disodium Hydrogen Phosphate

The specimen of salt used was three times recrystallized. By precipitation of the phosphorus as magnesium pyrophosphate, the exact strength of the mother solution was ascertained.

Table XXII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
16	164.3	68.4	215.3	68.2	268.5	67.3
32	182.4	75.9	238.7	75.6	298.9	74.9
128	212.1	88.3	278.4	88.2	350.9	87.9
512	231.6	96.4	304.7	96.5	384.6	96.4
1024	236.4	98.4	310.2	98.3	393.2	98.5
2048	240.3	100.0	315.6	100.0	399.0	100.0

Table XXIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
16	3.40	2.07	3.55	1.65
32	3.75	2.06	4.02	1.69
28	4.42	2.08	4.83	1.73
512	4.87	2.10	5.33	1.75
1024	4.92	2.08	5.53	1.78
2048	5.02	2.09	5.56	1.76

Potassium Chlorate

The specimen used was recrystallized and dried in an air bath for two hours at 120°. The strength of the mother solution was obtained by weighing the pure and dry salt.

Table XXIV.—Conductivity

V	0°	12°.5	25°	35°
8	58.9	80.8	104.7	124.9
32	64.3	88.3	115.2	137.3
128	68.5	94.2	122.8	146.5
512	70.1	96.7	126.1	150.9
1024	70.6	97.7	127.8	153.1
2048	71.2	98.4	128.4	154.0
4096	72.4	100.7	131.4	157.6

Table XXV.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.75	2.97	1.91	2.36	2.02	1.93
32	1.94	3.00	2.15	2.43	2.21	1.93
128	2.07	2.90	2.29	2.42	2.36	1.92
512	2.12	3.02	2.35	2.43	2.48	1.95
1024	2.15	3.04	2.42	2.47	2.52	1.97
2048	2.18	3.06	2.44	2.47	2.56	1.98
4096	2.25	3.09	2.46	2.44	2.62	1.98

Table XXVI.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	81.3	80.2	79.7	79.2
32	88.8	87.6	87.5	87.1
128	94.6	93.5	93.2	92.9
512	96.8	96.0	95.9	95.7
1024	97.5	97.2	97.2	97.1
2048	98.3	97.7	97.7	97.7
4096	100.0	100.0	100.0	100.0

Potassium Chlorate

The specimen of salt used for this series was the same as that used for the work at lower temperatures. It was purified and standardized in exactly the same way as above.

Table XXVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	125.4	78.3	158.6	77.6	192.1	76.8
32	137.3	85.8	173.4	84.9	211.9	84.8
128	146.4	91.4	185.0	90.6	228.8	91.6
512	151.2	94.4	193.4	94.6	239.1	95.7
1024	153.1	95.6	197.4	96.6	241.5	96.7
2048	158.1	98.7	200.8	98.2	244.9	98.0
4096	160.1	100.0	204.3	100.0	249.7	100.0

Table XXVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.22	1.77	2.23	1.40
32	2.41	1.76	2.57	1.48
128	2.57	1.76	2.92	1.57
512	2.81	1.85	3.05	1.57
1024	2.95	1.92	2.94	1.49
2048	2.85	1.80	2.94	1.46
4096	2.95	1.84	3.03	1.48

Potassium Perchlorate

This salt received two crystallizations. It was dried in the air bath for two hours at 130°.

Table XXIX.—Conductivity

V	0°	12°.5	25°	35°
32	65.1	89.8	116.9	139.6
128	68.9	95.0	125.1	149.5
512	71.7	98.2	129.0	154.2
1024	72.0	99.5	130.7	155.3
2048	73.3	101.2	132.6	158.6
4096	74.3	102.6	134.5	160.7

Table XXX.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	1.98	3.04	2.17	2.42	2.27	1.94
128	2.08	3.02	2.40	2.52	2.44	1.95
512	2.12	2.95	2.44	2.60	2.52	1.95
1024	2.20	3.05	2.49	2.50	2.56	1.95
2048	2.23	3.04	2.51	2.48	2.60	1.96
4096	2.26	3.04	2.55	2.49	2.62	1.94

Table XXXI.—Percentage Dissociation

V	0°	12°.5	25°	35°
32	87.6	87.6	86.9	86.9
128	92.7	92.5	93.0	93.0
512	96.5	95.7	95.9	95.3
1024	97.0	96.9	97.1	96.6
2048	98.6	98.5	98.5	98.6
4096	100.0	100.0	100.0	100.0

Potassium Perchlorate

The values given below were obtained from the same sample of salt as was used at lower temperatures. As before, it was recrystallized and dried in the air bath for two hours at 130°.

Table XXXII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
32	139.8	85.8	178.0	86.2	217.2	86.4
128	150.3	92.3	190.2	92.1	232.7	92.6
512	153.9	94.5	194.3	94.1	237.7	94.6
1024	155.0	95.1	195.9	94.9	240.6	95.7
2048	157.5	96.7	200.0	96.9	244.2	97.2
4096	162.9	100.0	206.4	100.0	251.3	100.0

The conductivity values given by Ostwald for this salt are several units higher than those here recorded. Several of the above values were redetermined with a new specimen of pure potassium perchlorate, and very close agreements with the above values were obtained.

Table XXXIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	2.55	1.81	2.61	1.46
128	2.66	1.77	2.83	1.48
512	2.69	1.75	2.89	1.48
1024	2.73	1.76	2.98	1.52
2048	2.83	1.79	2.94	1.42
4096	2.90	1.78	2.99	1.44

Potassium Phosphate

The phosphorus content of the original solution was determined by means of magnesia mixture. Different specimens from Kahlbaum were used for the low and high temperature work.

Table XXXIV.—Conductivity

V	0°	12°.5	25°	35°
8	116.6	163.8	217.2	263.6
32	144.1	206.7	280.3	344.2
128	178.9	257.7	348.2	425.2
512	193.7	274.7	366.1	442.8
1024	192.1	271.5	362.5	440.1
2048	190.0	268.3	359.3	437.2
4096	179.0	252.0	336.7	407.6

Table XXXV.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	3.78	3.24	4.27	2.60	4.64	2.13
32	5.00	3.54	5.88	2.85	6.39	2.24
128	6.30	3.50	7.24	2.81	7.70	2.21
512	6.48	3.34	7.31	2.66	7.67	2.10
1024	6.35	3.30	7.28	2.68	7.76	2.14
2048	6.26	3.29	7.28	2.75	7.79	2.14
4096	5.84	3.27	6.78	2.69	7.09	2.10

Table XXXVI.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	60.2	59.6	59.3	59.5
32	74.4	75.2	76.5	77.7
128	92.9	93.8	95.1	96.0
512	100.0	100.0	100.0	100.0
1024	99.2	98.8	99.0	99.3
2048	98.0	97.3	98.1	98.7
4096	92.4	92.1	91.9	92.0

Potassium Phosphate

Table XXXVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	261.4	59.5	334.5	58.2	415.5	58.7
32	346.9	77.7	453.6	78.7	566.1	80.0
128	427.8	96.0	552.2	96.1	685.7	96.9
512	443.7	100.0	574.6	100.0	707.6	100.0
1024	439.8	99.3	565.1	98.3	697.3	98.5
2048	426.0	98.7	549.5	95.6	676.2	95.5
4096	402.5	92.0	517.1	90.0	646.9	91.4

Table XXXVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	4.73	1.79	5.40	1.61
32	7.29	2.04	7.50	1.65
128	8.46	1.99	8.90	1.61
512	8.78	1.98	8.87	1.54
1024	8.33	1.89	8.81	1.56
2048	7.49	1.71	8.45	1.53
4096	7.30	1.81	8.65	1.67

Calcium Chloride

The specimen of salt used was purified by two recrystallizations from conductivity water. The concentration of the mother solution was ascertained by weighing calcium as the oxide, CaO.

Table XXXIX.—Conductivity

V	0°	12°.5	25°	35°
2	80.5	109.6	142.1	169.1
8	95.3	132.1	172.5	207.4
32	106.4	149.3	197.5	238.0
128	117.8	165.6	219.2	265.8
512	124.0	174.8	232.4	281.9
1024	126.5	179.0	236.1	284.6
2048	131.4	185.0	245.0	298.3
4096	131.3	185.2	246.5	300.0

Table XL.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
2	2.32	2.90	2.60	2.46	2.70	1.90
8	2.94	3.08	3.23	2.44	3.49	2.02
32	3.43	3.21	3.85	2.58	4.05	2.05
128	3.82	3.24	4.29	2.58	4.66	2.12
512	4.06	3.27	4.57	2.61	4.94	2.12
1024	4.20	3.39	4.70	2.68	4.85	2.05
2048	4.28	3.02	4.80	2.58	5.33	2.17
4096	4.31	3.26	4.90	2.59	5.35	2.17

Table XLI.—Percentage Dissociation

V	0°	12°.5	25°	35°
2	61.2	59.1	57.6	56.3
8	72.5	71.3	69.9	69.1
32	80.9	80.6	80.1	79.3
128	89.6	89.4	88.9	88.6
512	94.3	94.2	94.6	93.9
1024	96.2	96.1	95.7	94.8
2048	100.0	100.0	99.3	99.4
4096	99.9	99.9	100.0	100.0

Strontium Chloride

After the salt had been subjected to three recrystallizations the chlorine content in the mother solution was determined as silver chloride.

Table XLII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	208.9	68.8	265.5	67.7	324.4	66.6
16	224.5	73.9	285.6	72.8	350.2	71.9
32	240.4	79.1	305.7	77.9	377.5	77.5
128	267.3	88.0	342.4	87.3	424.6	87.2
512	282.8	93.1	367.7	93.7	453.9	93.2
1024	286.8	94.4	373.0	95.1	463.3	95.2
2048	297.0	97.8	383.2	97.7	476.5	97.8
4096	303.7	100.0	392.2	100.0	486.9	100.0

Table XLIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	3.78	1.81	3.92	1.48
16	4.07	1.81	4.25	1.49
32	4.35	1.81	4.79	1.56
128	5.01	1.87	5.48	1.60
512	5.66	2.00	5.75	1.57
1024	5.75	2.01	6.02	1.62
2048	5.75	1.94	6.22	1.62
4096	5.90	1.94	6.32	1.61

Barium Bromide

After careful recrystallization of the salt, the exact barium content in the mother solution was determined as barium sulphate.

Table XLIV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	222.0	70.5	280.1	69.2	340.1	68.4
16	237.8	75.6	301.1	74.4	367.6	73.9
32	251.8	80.0	320.2	79.1	392.8	79.0
128	278.4	88.5	358.0	88.5	439.2	88.3
512	295.1	93.8	379.6	93.8	467.6	94.0
1024	302.1	96.0	385.3	95.2	475.1	95.5
2048	305.5	97.1	393.9	97.4	484.6	97.4
4096	314.7	100.0	404.5	100.0	497.2	100.0

Table XLV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	3.87	1.74	4.00	1.42
16	4.22	1.77	4.43	1.47
32	4.56	1.81	4.84	1.51
128	5.31	1.91	5.41	1.51
512	5.63	1.91	5.87	1.54
1024	5.55	1.83	5.99	1.55
2048	5.90	1.93	6.05	1.54
4096	5.65	1.80	6.18	1.53

Barium Formate

The above salt was three times recrystallized. The concentration of the barium in the original solution was determined by weighing the barium as barium sulphate.

Table XLVI.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	158.8	66.1	201.0	64.2	245.4	63.6
16	178.4	74.3	227.3	72.6	275.1	71.4
32	196.6	81.9	252.1	80.5	307.3	79.7
128	225.4	93.8	289.6	92.4	359.6	93.3
512	237.8	99.0	308.2	98.4	383.6	99.5
1024	240.1	100.0	313.2	100.0	385.5	100.0
2048	239.8	99.9	309.5	98.8	376.4	97.6

Table XLVII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	2.81	1.77	2.96	1.47
16	3.26	1.83	3.19	1.43
32	3.70	1.88	3.68	1.46
128	4.28	1.89	4.67	1.61
512	4.69	1.97	5.03	1.63
1024	4.87	2.03	4.82	1.54
2048	4.65	1.94	4.46	1.44

Magnesium Chloride

The above salt was purified by three crystallizations. Precipitations of the magnesium as magnesium pyrophosphate determined the strength of the mother solution.

Table XLVIII.—Conductivity

V	0°	12°.5	25°	35°
4	80.2	112.1	147.3	177.6
8	87.6	123.2	162.1	196.1
32	100.0	141.1	187.1	226.4
128	110.2	156.1	208.0	252.4
512	115.7	164.3	219.4	266.8
1024	118.3	168.5	225.0	272.2
2048	120.2	172.8	230.2	280.0
4096	123.5	176.3	234.7	285.2

Table XLIX.—Temperature Coefficients

	0°–12°.5		12°.5–25°		25°–35°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.55	3.17	2.82	2.51	3.03	2.05
8	2.85	3.25	3.11	2.52	3.40	2.09
32	3.29	3.29	3.68	2.60	3.93	2.10
128	3.67	3.33	4.15	2.65	4.44	2.13
512	3.89	3.36	4.41	2.67	4.74	2.16
1024	4.02	3.39	4.52	2.68	4.72	2.09
2048	4.21	3.48	4.59	2.65	4.98	2.16
4096	4.22	3.32	4.67	2.64	5.05	2.15

Table L.—Percentage Dissociation

V	0°	12°.5	25°	35°
4	64.9	63.6	62.8	62.3
8	70.9	69.9	69.1	68.7
32	80.9	80.0	79.7	79.4
128	89.2	88.5	88.6	88.5
512	93.7	93.2	93.5	93.5
1024	95.8	95.6	95.8	95.4
2048	97.3	98.0	98.1	98.2
4096	100.0	100.0	100.0	100.0

Magnesium Sulphate

This salt was recrystallized three times. An attempt was made to get the purified and dried product anhydrous by heating it in an air bath for two hours at 225°. It was found that the anhydrous salt readily took up moisture from the air, and, furthermore, that the salt could not be obtained perfectly anhydrous at temperatures even higher than that stated above. Consequently, the mother solution was standardized by analysis, the sulphur being precipitated as barium sulphate.

Table LI.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	72.4	27.6	90.5	26.5	106.5	25.2
8	104.0	39.6	131.0	38.3	155.4	36.8
16	120.4	45.8	150.7	44.1	179.0	42.4
32	139.0	52.9	174.6	51.1	208.6	49.4
128	180.7	68.8	230.3	67.4	279.1	66.0
512	224.7	85.6	288.1	84.3	353.1	83.6
1024	245.9	93.6	317.7	93.0	395.4	93.6
2048	262.6	100.0	341.7	100.0	422.6	100.0

Table LII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	1.21	1.67	1.07	1.18
8	1.80	1.73	1.63	1.24
16	2.02	1.68	1.89	1.27
32	2.37	1.71	2.27	1.30
128	3.31	1.83	3.25	1.41
512	4.23	1.88	4.32	1.50
1024	4.79	1.95	5.18	1.63
2048	5.27	2.01	5.39	1.58

Manganous Chloride

After the salt had been twice recrystallized from conductivity water, the manganese in the original solution was determined as the pyrophosphate.

Table LIII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	142.5	49.3	177.3	47.5	210.5	44.9
8	191.5	66.3	242.3	64.9	293.7	62.7
16	210.3	72.8	266.8	71.5	326.6	69.7
32	226.5	78.4	289.1	77.5	357.0	76.2
128	252.9	87.6	325.0	87.2	402.3	85.9
512	274.7	95.1	356.2	95.5	447.4	95.5
1024	281.3	97.4	366.4	98.3	459.2	98.1
2048	288.8	100.0	372.9	100.0	468.4	100.0

Table LIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.32	1.63	2.21	1.25
8	3.38	1.76	3.43	1.41
16	3.77	1.79	3.99	1.49
32	4.17	1.88	4.53	1.57
128	4.81	1.90	5.15	1.59
512	5.43	1.97	6.08	1.71
1024	5.67	2.01	6.19	1.79
2048	5.61	1.94	6.37	1.71

Manganous Nitrate

This salt was once recrystallized, care being taken to prevent decomposition. The manganese was determined as manganese pyrophosphate.

Table LV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	139.6	52.0	171.5	49.3	205.0	47.5
8	183.8	68.5	231.7	67.0	279.9	64.8
32	216.8	80.8	277.0	80.0	338.8	78.5
128	242.0	90.2	310.5	89.7	382.8	88.7
512	256.5	95.8	335.0	96.8	413.5	95.8
1024	264.7	98.7	341.3	98.6	425.4	98.6
2048	268.3	100.0	346.3	100.0	431.5	100.0

Table LVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.13	1.53	2.23	1.30
8	3.19	1.73	3.21	1.39
32	4.01	1.85	4.12	1.49
128	4.57	1.89	4.82	1.55
512	5.20	2.02	5.23	1.56
1024	5.11	1.93	5.61	1.64
2048	5.20	1.94	5.68	1.64

Aluminium Chloride

The specimen of salt used was not recrystallized. It was, however, tested for sulphates and nitrates with negative results. The test for iron disclosed a mere trace of that element. It was only by using a fairly large amount of the substance that a positive result was obtained.

Table LVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
4	231.6	45.8	296.9	42.2	361.4	37.9
8	266.8	52.8	341.6	48.6	419.1	44.0
16	291.6	58.6	381.1	54.2	470.9	49.4
64	350.3	69.3	455.5	64.8	567.3	59.5
512	429.3	85.0	567.5	80.7	730.0	76.6
1024	449.8	89.1	609.3	86.6	796.7	83.6
2048	479.9	95.0	647.5	92.1	868.5	91.1
4096	505.1	100.0	703.2	100.0	953.2	100.0

Table LVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	4.35	1.88	4.30	1.45
8	4.99	1.87	5.16	1.51
16	5.66	1.91	5.99	1.58
64	7.02	2.00	7.45	1.62
512	9.22	2.15	10.83	1.91
1024	10.63	2.36	12.49	2.05
2048	11.17	2.33	14.73	2.27
4096	13.21	2.62	16.66	2.37

Aluminium Nitrate

The salt used was a fine specimen obtained from Kahlbaum. Recrystallization was effected by desiccation over sulphuric acid. The powdered salt was then allowed to stand in a vacuum over potassium hydroxide for several days. The aluminium in the mother solution was determined as aluminium oxide.

Table LIX.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
4	219.0	45.7	276.0	42.0	338.6	37.3
8	252.0	52.6	320.8	48.8	393.9	43.4
32	306.3	64.0	394.3	60.0	487.3	53.6
128	358.0	74.7	464.4	70.7	583.9	64.3
512	407.2	85.0	535.8	82.0	685.9	75.5
1024	433.9	90.6	575.8	87.7	750.5	82.6
2048	457.4	95.5	613.3	93.4	820.9	90.4
4096	478.9	100.0	656.6	100.0	908.2	100.0

Table LX.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	3.80	1.73	4.17	1.51
8	4.57	1.81	4.87	1.52
32	5.87	1.92	6.20	1.57
128	7.10	1.98	7.97	1.72
512	8.84	2.14	10.07	1.88
1024	9.46	2.18	11.65	2.01
2048	10.40	2.27	13.84	2.25
4096	11.86	2.47	16.77	2.55

Aluminium Sulphate

The above salt was recrystallized by slowly desiccating a saturated solution over sulphuric acid. The exact strength of the mother solution was ascertained by determining the sulphur as barium sulphate.

Table LXI.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
4	114.2	16.5	136.5	14.6	152.8	12.5
8	141.3	20.4	166.7	17.8	185.7	15.2
32	198.9	28.7	236.7	25.3	266.2	21.8
128	278.3	40.1	339.9	36.3	395.1	32.4
512	395.5	57.0	497.3	53.1	594.6	48.7
1024	478.2	68.9	613.2	65.5	740.2	60.6
2048	571.7	82.4	746.8	79.8	943.0	72.2
4096	693.5	100.0	936.1	100.0	1221.2	100.0

Table LXII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	1.49	1.22	1.09	0.8
8	1.69	1.20	1.27	0.76
32	2.52	1.27	1.97	0.83
128	4.11	1.48	3.67	1.08
512	6.79	1.72	6.49	1.31
1024	9.00	1.88	8.47	1.38
2048	11.67	2.04	13.08	1.75
4096	16.17	2.33	19.01	2.03

Chromic Chloride (Violet Variety)

The sample of the above salt was secured from Kahlbaum, and it was purified by recrystallization from conductivity water. This was effected by the slow desiccation of a saturated solution over sulphuric acid. The powdered salt was afterwards dried over potassium hydroxide in a vacuum desiccator for a period of about a week. A gravimetric determination of the chromium as chromic oxide gave the exact strength of the original solution.

Table LXIII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	256.7	41.0	332.3	39.7	410.0	37.2
32	330.5	52.7	431.2	51.6	538.5	48.9
128	406.0	64.8	534.3	63.9	681.5	61.9
512	486.5	77.6	650.9	77.9	834.4	75.7
1024	543.7	86.7	724.2	86.6	941.3	85.5
2048	582.8	93.0	783.9	93.8	1015.7	92.2
4096	626.7	100.0	836.5	100.0	1101.4	100.0

Table LXIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	5.04	1.96	5.18	1.56
32	6.71	2.03	7.15	1.66
128	8.55	2.11	9.81	1.83
512	10.96	2.25	12.23	1.87
1024	12.03	2.21	14.47	1.99
2048	13.42	2.30	15.45	1.53
4096	13.99	2.23	17.66	1.60

Chromic Nitrate (Violet Variety)

This salt was recrystallized by allowing a concentrated solution to desiccate over phosphorus pentoxide. The chromium content of the mother solution was determined as chromic oxide.

Table LXV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	180.4	32.1	231.8	30.2	278.5	27.9
8	260.3	46.4	335.9	43.8	416.3	41.7
16	292.5	52.1	380.6	49.6	473.8	47.4
32	322.1	57.4	420.5	54.8	531.2	53.2
128	388.2	69.1	511.2	66.6	658.9	65.9
512	472.2	84.1	634.7	82.7	821.2	82.2
1024	514.7	91.7	692.0	90.2	894.4	89.5
2048	561.5	100.0	767.0	100.0	999.0	100.0

Table LXVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	3.43	1.90	3.11	1.34
8	5.04	1.93	5.36	1.59
16	5.87	2.01	6.22	1.63
32	6.76	2.09	7.38	1.75
128	8.20	2.11	9.85	1.92
512	10.83	2.29	12.43	1.96
1024	11.82	2.32	13.49	1.95
2048	13.70	2.44	15.47	2.01

Chromic Sulphate (Violet Variety)

This salt was recrystallized by slow desiccation of a concentrated solution over sulphuric acid. The powdered salt was afterwards dried in a vacuum over potassium hydroxide. The chromium in the original solution was determined as chromic oxide. The conductivity values obtained not agreeing with those of other investigators, it was deemed advisable to redetermine the chromium in the mother solution. This was done and a very good agreement with the results of the previous analysis was obtained.

Table LXVII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_V	α	μ_V	α	μ_V	α
8	110.4	19.3	128.1	14.5	139.9	12.4
32	179.0	31.3	209.7	23.8	228.5	20.2
128	265.5	46.5	328.0	37.2	370.6	32.7
512	362.2	63.4	488.8	55.5	585.3	51.7
1024	418.9	73.3	585.4	66.5	732.1	64.6
2048	458.8	80.3	713.3	80.9	905.2	80.0
4096	571.2	100.0	880.9	100.0	1132.4	100.0

Table LXVIII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.18	1.07	0.79	0.62
32	2.05	1.14	1.25	0.60
128	4.17	1.57	2.84	0.86
512	8.44	2.33	6.43	1.32
1024	11.10	2.65	9.78	1.67
2048	16.97	3.69	12.79	1.78
4096	20.65	3.61	16.77	1.94

Lead Nitrate

The specimen of salt used was twice recrystallized. The purified product was dried to constant weight in the air bath at about 120°. A weighed amount of salt gave the exact concentration of the mother solution.

Table LXIX.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	111.5	36.0	143.0	35.9	175.9	35.8
8	170.2	54.9	218.4	54.8	267.8	54.5
16	196.6	63.5	251.7	63.2	309.4	62.9
32	220.4	71.2	281.6	70.8	347.8	70.7
128	261.0	84.3	333.3	83.8	410.2	83.4
512	291.0	93.9	369.6	92.9	455.0	92.5
1024	300.0	96.9	385.1	96.8	477.7	97.2
2048	309.6	100.0	397.9	100.0	491.8	100.0

Table LXX.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.10	1.88	2.19	1.53
8	3.21	1.88	3.29	1.51
16	3.74	1.93	3.85	1.53
32	4.08	1.81	4.41	1.53
128	4.83	1.85	5.13	1.53
512	5.24	1.80	5.69	1.54
1024	5.67	1.89	6.17	1.60
2048	5.89	1.90	6.36	1.64

Nickel Nitrate

This salt was purified by three recrystallizations. The nickel content of the mother solution was ascertained by driving off the oxides of nitrogen and reducing the nickel oxide to constant weight in a stream of hydrogen.

Table LXXI.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
2	145.5	50.9	182.7	49.4	219.7	48.4
8	188.8	66.0	239.5	64.8	291.9	64.3
32	218.4	76.4	278.3	75.3	342.7	75.7
128	243.6	85.2	310.6	84.0	386.1	85.0
512	262.0	91.7	336.2	91.0	416.0	91.6
1024	267.6	93.6	344.6	93.2	427.3	94.1
2048	285.8	100.0	369.8	100.0	453.9	100.0
4096	281.2	98.4	364.1	98.5	449.8	99.1

Table LXXII.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
2	2.48	1.70	2.47	1.35
8	3.38	1.78	3.49	1.42
32	3.99	1.82	4.29	1.54
128	4.47	1.83	5.03	1.65
512	4.95	1.88	5.32	1.58
1024	5.13	1.92	5.53	1.60
2048	5.60	1.96	5.61	1.52
4096	5.53	1.97	5.72	1.57

Copper Ammonium Sulphate

After one recrystallization the sulphuric acid content in the above salt was accurately determined by means of barium chloride.

Table LXXIII.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
4	225.2	36.9	278.3	35.3	334.7	35.6
8	260.0	42.7	323.5	41.0	383.1	39.2
32	333.6	54.7	417.5	53.0	496.9	50.9
128	416.9	68.4	521.1	66.1	630.1	64.5
512	499.7	82.0	634.0	80.4	768.9	78.7
1024	546.8	89.7	697.8	88.5	850.8	87.1
2048	578.3	94.9	744.1	94.4	916.2	93.8
4096	609.5	100.0	788.3	100.0	976.8	100.0

Table LXXIV.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
4	3.54	1.57	3.76	1.35
8	4.23	1.63	3.97	1.23
32	5.59	1.67	5.29	1.26
128	6.96	1.66	7.27	1.39
512	8.95	1.79	8.99	1.42
1024	10.67	1.95	10.20	1.46
2048	11.05	1.94	11.47	1.54
4096	11.92	1.95	12.57	1.59

Uranyl Sulphate

As there was only a small quantity of this salt available, it was not purified. After several days' drying in a vacuum over

potassium hydroxide, the uranium in the mother solution was determined as the oxide, U_3O_8.

Table LXXV.—Conductivity and Dissociation

	35°		50°		65°	
V	μ_v	α	μ_v	α	μ_v	α
8	153.0	33.2	172.5	30.2	189.9	28.4
32	192.3	41.7	215.3	37.7	231.0	34.6
128	248.6	53.9	279.5	49.0	300.1	44.9
512	322.1	69.8	369.5	64.7	403.7	60.4
1024	360.9	78.2	421.7	73.9	471.0	70.5
2048	413.5	89.6	498.9	87.4	562.6	84.2
4096	461.4	100.0	570.7	100.0	667.9	100.0

Table LXXVI.—Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	1.30	0.85	1.16	0.67
32	1.53	0.79	1.05	0.49
128	2.06	0.83	1.37	0.49
512	3.16	0.98	2.28	0.62
1024	4.05	1.12	3.29	0.78
2048	5.69	1.13	4.25	0.85
4096	7.29	1.23	6.48	1.14

SPECIAL WORK

The conductivity data for chromium salts, as is also the case with other salts which are strongly hydrated and hydrolyzed, are so discordant that it was decided to do some special work on such salts. It was hoped to arrive at a possible explanation for the discordant results obtained by different investigators.

Insolubility of Jena Glass

The vessels which held the solutions used in this work were of Jena glass. As far as the solvent action of water on the glass is concerned, it is evident that by treating them in the following way all soluble matter can be removed from them up to temperatures as high as 90°. A chromic acid cleaning mixture had stood in the vessels all summer. After rinsing, they were filled with distilled water, tightly corked, and warmed to 90° for eight hours. Two of the bottles were

carefully rinsed and filled with pure water whose conductivity was known. The stoppers were tightly wired into place, and the two bottles containing the water were warmed to 90° for four hours. They were allowed to stand for two days at room temperature, and then the conductivities of the two specimens of water were determined. The results are seen best when expressed as follows: R is the resistance in the rheostat and A the reading on the bridge.

Reading for unheated water at 25°

$$R = 2000, A = 515$$

Readings at 25° for the water which had been heated in bottles to 90° for four hours

$$(1)\ R = 3000, A = 520$$
$$(2)\ R = 2000, A = 517$$

From these results and others carried out in an analogous manner, it was concluded that practically all soluble matter had been removed from our vessels.

A Dehydrolytic Time Factor in the Case of Chromic Salts

The study of the green and violet varieties of chromic salts has long been a favorite subject of investigation. The conductivity method[1] shows that the violet variety has a smaller conductivity than the corresponding concentration of the green variety, and that with increase in dilution, the conductivity of the violet salt increases at a greater rate than that of the green. To explain the greater conductivity of the green modification, several theories have been advanced. The one generally accepted to-day, and substantiated by the work of Recoura,[2] Whitney,[3] Denham,[4] Graham,[5] and others, is that the green variety contains some of the violet variety plus the products of its hydrolysis—a complex chromium salt and the corresponding acid. If this is true, the law of mass action would explain why the conductivity of the violet variety increases more rapidly with dilution than the green variety.

[1] Carnegie Institution of Washington, Publication No. **170**, p. 35.
[2] Ann. chim. phys., [7] **4**, 494 (1895).
[3] Z. physik. Chem., **20**, 40 (1896).
[4] Z. anorg. Chem., **57**, 361 (1908).
[5] This Journal, **48**, 145 (1912).

For those salts which are hydrolyzed by rise in temperature, it was seen that unless the products of hydrolysis recombine as the temperature is lowered our method for the purification of salts for conductivity measurements must be changed. This point was tested out for the chromic salts.

A specimen of violet chromic chloride secured from Kahlbaum was recrystallized by allowing a solution saturated at room temperature to desiccate over phosphorus pentoxide. The chromium content of the mother solution was determined as the oxide Cr_2O_3. From the mother solution, N/32 and N/512 solutions were prepared. Four of the bottles, treated as above described to remove soluble matter, were filled with the N/32 chromic chloride solution. The stoppers of three of them were tightly wired into place. The first was warmed to 50° for two hours, the second to 65° for two hours, the third to 90° for two hours. The fourth was not heated. The heated solutions were quickly cooled to room temperature, and their conductivities determined at 35°, 50° and 65°, along with the solution which had not been heated. The following results were obtained:

V	*t*	Not heated	Heated to 50°	Heated to 65°	Heated to 90°
32	35°	330.5	331.4	342.0	415.9
32	50°	424.6	429.7	439.0	519.0
32	65°	532.4	536.9	544.6	624.2

The same process was repeated with the N/512 chromium chloride solution.

V	*t*	Not heated	Heated to 50°	Heated to 65°	Heated to 90°
512	35°	487.4	489.5	500.6	559.7
512	50°	652.2	656.7	667.7	724.6
512	65°	842.5	843.8	856.6	915.1

The results for the more dilute solutions are of the same character as those for the more concentrated. They indicate that the hydrolysis of chromium salts increases rapidly with rise in temperature. Its effect is very marked even in the N/32 solution. If we subtract the conductivities of the solutions which were not heated from the conductivities of the solutions

which were heated to 90°, we note that the effect of hydrolysis, considering the amount of salt present in the two solutions, is very much more marked in the case of the more dilute solution.

N/32 $CrCl_3$	N/512 $CrCl_3$
35° 85.4	35° 72.3
50° 94.4	50° 72.4
65° 91.8	65° 72.6

Furthermore, it is evident that the increase in hydrolysis, at least for the N/512 solution of chromic chloride, is fairly constant, regardless of the temperature at which the conductivity readings were taken. This points to the conclusion that dehydrolysis did not take place to any appreciable extent as the solution was cooled down, and that as the temperature was again raised the conductivity of the green variety increased at about the same rate as the conductivity of the violet variety.

The following experiment was carried out to throw some light on the length of time required for the products of hydrolysis to recombine:

The N/512 solution of chromic chloride which had been heated to 90° for two hours was allowed to stand at room temperature for twenty days, and its conductivity again determined at 35°. The value found was 508, while the value found shortly after heating was 559.7. The unheated solution gave a conductivity of 487.4. A similar experiment with N/512 chromic chloride was carried out. The solution had been heated to 90° for two hours, and allowed to stand at room temperature for twenty days. Its conductivity was determined at 65°, and the value 885 was found. The conductivity shortly after heating was 915.1. That of the unheated solution was 842.5. Here we evidently have a dehydrolytic time factor which persists for days and perhaps months. From these results it is concluded that, in the purification of chromic salts, great care must be taken to keep the temperature of the solution lower than the lowest temperature at which conductivity readings are to be made. The discordant values obtained by previous investigators are perhaps due to their

method of purification and failure to take into account the dehydrolytic time factor.

Evidently, it is a matter of great importance for conductivity methods to determine whether other salts which are easily hydrolyzed show a similar phenomenon. The method by which a salt is ordinarily purified is to cool quickly a solution which is saturated at a certain high temperature. In warming solutions of such salts, it is conceivable from the previous work that, upon crystallization, they might take out of solution an excess of one of the products of hydrolysis, if the acid and base did not immediately recombine as the solution was cooled. In view of the fact that it is just such kinds of salts that have been giving trouble in conductivity measurements, it seemed desirable to carry out the following experiments:

A specimen of aluminium sulphate from Kahlbaum was recrystallized by allowing a solution saturated at room temperature to desiccate over phosphorus pentoxide. The sulphuric acid in the original solution was determined as barium sulphate. Two bottles were filled with a N/32 solution, and two more with a N/512 solution. One bottle containing the N/32 solution and another containing the N/512 solution were securely stoppered, and both warmed to 85° for two hours. These solutions were quickly cooled to room temperature and their conductivities determined as soon as possible at 35°.

Aluminium Sulphate

V	*t*	Not heated	Heated to 85°
32	35°	205.8	206.4
512	35°	413.6	417.0

A similar experiment was carried out with magnesium chloride. The salt was purified by recrystallization from water, and the magnesium in the mother solution weighed as magnesium pyrophosphate. Two bottles, one containing the N/32 solution, the other containing the N/512 solution, were heated to 85° for $^1/_2$ hour. Both were tightly stoppered. They were quickly cooled to room temperature, and their conductivities determined at 25°.5, along with two other solutions which had not been heated.

Magnesium Chloride

V	*t*	Not heated	Heated to 85°
32	25.5	187.6	188.7
512	25.5	222.7	222.5

Other salts were worked with, and results of the same general character were obtained. These results point to the conclusion that it is usually safe to heat a salt during its purification almost up to the temperature at which it will decompose without influencing the conductivity readings. The only exception to this rule which was encountered applies to the chromic salts existing in two modifications. Of course, the hydrolysis of these salts is somewhat different from that of the ordinary salts.

The Water Correction as Influenced by Various Conditions

The conductivity of the water used in making up the solutions, when multiplied by the number expressing the volume of the solution, gives the water correction which must be subtracted from the molecular conductivity of the solution to obtain the true molecular conductivity of the salt in question. It is evident that any condition influencing the conductivity of the water will have an appreciable effect when multiplied by such numbers as 2048 and 4096. It is at these dilutions that the salt is assumed to be completely dissociated, and, consequently, an erroneous water correction would vitiate the μ_∞ values for the salt, and therefore its percentage dissociation. In the following experiments, several factors influencing the water correction were taken into account.

A. The water cell filled with conductivity water flowing at a rapid rate during a time when the air conditions in the room were much better than the normal conditions. The conductivity of the water was determined at 35° and the correction factors worked out for dilutions of N/1024, N/2048 and N/4096.

V	Correction
1024	1.74
2048	3.47
4096	6.95

B. Conductivity water was allowed to flow into a clean beaker at a rapid rate. The water was then exposed to the air for about three minutes at a time when the air conditions in the room were about normal. The time of exposure is somewhat less than the time required for making up a dilute solution and transferring it to the cell. The correction factors at 35° in this case were:

V	
1024	1.78
2048	3.56
4096	7.12

C. For this experiment, the air in the room was made less pure than normal. Three Bunsen burners were lighted for fifteen minutes, also a bottle containing ammonium hydroxide and another containing hydrochloric acid had been uncorked for an instant. The water was allowed to drop into the water cell so that a large surface of the water would be exposed to the air. The cell, holding about 60 cc., was filled during the course of two minutes. On the average a burette is hardly drained during that time. The correction factors at 35° were:

V	
1024	2.34
2048	4.68
4096	9.35

This work was repeated and results of a very similar character were obtained.

It is evident from the above work that errors larger than a per cent. may be introduced into conductivity work unless the proper water corrections are applied. The purity of the air in the room, during the times at which solutions are made up and the water cell filled, should be about the same. Furthermore, to obtain comparable results, the filling of the water cell should be so carried out that the water is exposed to the air for about the same period of time, and under the same conditions, as the more dilute solutions. These factors are more important for accurate conductivity work than has hitherto been realized. If the air conditions in the room were

good at the time the water cell was filled, and bad at the time the solutions were made up, the μ_∞ values would be too large, and too small when the reverse conditions exist. In this laboratory care is taken to have the air conditions always about the same, and the air as free from impurities as possible.

Dissociation as Measured by the Kohlrausch Conductivity Method

It is generally believed that the dissociation values, as obtained by the conductivity method, for salts which are not hydrated and hydrolyzed are correct to within the limits of experimental error. Of course, if a strongly concentrated solution of such a salt was used, the effect of viscosity would interfere with the velocities of the ions, and, consequently, the observed dissociation. It has been noted in this work that a great majority of the salts worked with did not reach complete dissociation even at a dilution of $V = 4096$. An attempt to work at dilutions beyond this proved to be impractical. Large experimental errors are involved in working with such small quantities of substance, and the effect of the air conditions on the water correction is very great.

It was noted, from the dissociation values obtained in this work, that the percentage difference between the μ_∞ value and the molecular conductivity of the next more dilute solution, as a rule, showed an increase with rise in temperature.

To throw more light upon the correctness of the above observation, some carefully prepared solutions of salts but little hydrolyzed and hydrated in dilute solutions were used. They were pure sodium chloride and pure sodium perchlorate. Special care was taken, as has already been explained, to apply the proper water correction.

For sodium chloride the following results were noted:

V	0°	12°.5	25°	35°
512	62.3	...	...	...
1024	63.2	88.6	116.9	142.6
2048	63.4	89.5	118.4	143.8
4096	63.6	90.2	120.0	145.5

The results for sodium perchlorate are very similar. They have already been tabulated (Table XVII).

It is evident that, as the temperature rises, the percentage increase in conductivity obtained by subtracting from the μ_∞ value the molecular conductivity of the next more dilute solution slowly becomes greater. We have reached with certainty the μ_∞ value only at 0°. For higher temperatures, it is necessary to work at greater dilutions to obtain the true μ_∞ value, and this, as we have seen, is impractical.

What is here brought out on a small scale becomes much more pronounced for salts which are strongly hydrated and hydrolyzed. The chromium and aluminium compounds illustrate this point very well (see Tables LXII to LXIX, inclusive).

If the salt does not reach a decided μ_∞ value at 0° for a dilution $V = 4096$, it is less probable that it will at any higher temperature, if for no other reason than because with rise in temperature the association of the solvent and its dielectric constant become less, and consequently its dissociating power is less. If the salt is strongly hydrolyzed or polymerized, the further removed from the true μ_∞ value will be the μ_v value obtained at a dilution $V = 4096$. Generally, in the dilute solutions, rise in temperature very greatly increases the effect of any one of these factors, and causes the true μ_∞ value to become more and more removed from the μ_v value obtained at a dilution $V = 4096$.

Hydrolysis is probably the chief factor in making it appear that a salt is not completely dissociated in our very dilute solutions. Aqueous solutions of many salts show an acid or basic reaction at ordinary temperatures. If we consider the case of ammonium chloride dissociated into ammonia and hydrochloric acid gas at high temperatures, we perhaps have a picture of how a strong acid and strong base in aqueous solution may exist in equilibrium with the salt molecules and water at high temperatures. As is well known, the effect of dilution and rise in temperature is to increase the hydrolysis. Consequently, at high temperatures to reach that point where there is no further increase in conductivity, it would be necessary to work with exceedingly dilute solutions. A large number of salts are but little hydrolyzed or polymerized in dilute solutions, and in such cases we can reach μ_∞ values

which are close to the correct ones. The presence of hydrated ions would necessarily make the observed dissociation too low. It does not seem probable that conductivity methods will, in the near future, be modified so that we can measure accurately the dissociation of salts strongly hydrated, hydrolyzed or polymerized. As a means of studying solutions, and obtaining the dissociation of electrolytes neither strongly hydrated, hydrolyzed nor polymerized, the conductivity method has been and probably will continue to be of great service.

DISCUSSION OF THE CONDUCTIVITY TABLES

Conductivities

Several of the salts studied in this investigation showed conductivities that are very interesting. Perhaps most interesting of all is that of ammonium acid sulphate. It is a ternary salt showing small dissociation in concentrated solutions. Its exceptionally high conductivity is probably due to the presence of the hydrogen ion. Because of small hydration, hydrolysis and depolymerization in concentrated solutions its conductivity is little increased by rise in temperature. At a dilution $V = 32$, hydrolysis and depolymerization evidently become very marked, and from then on its conductivity increases rapidly with rise in temperature and increase in dilution.

The high conductivity of potassium phosphate cannot fail to attract attention. It is a quaternary electrolyte strongly dissociated in concentrated solutions. Evidently, its complex ions break down in concentrated solutions, causing considerable hydrolysis. At the dilution $V = 512$ there is no further increase in conductivity with rise in temperature and increase in dilution. This is the only salt studied that gave clean cut μ_∞ values. It should be noted that it crystallizes without water, and, therefore, is but little hydrated in solution, and that the breaking down of its complex ions, giving rise to hydrolysis, produces its maximum effect in fairly concentrated solutions.

The conductivities of the aluminium and chromium compounds are very high and strikingly similar. The presence of a large number of ions, hydration and hydrolysis, condition

the large conductivity of these salts. The conductivity of aluminium sulphate in concentrated solutions is much less than that of either the nitrate or chloride. The same applies to the chromium salt, as does also the following. In dilute solutions, probably due to depolymerization and hydrolysis, the conductivity of the sulphates is much greater than that of the chlorides or nitrates.

Due to the greater weight of the anion and the smaller degree of dissociation, the conductivity of sodium chlorate is less than that of sodium chloride. That of sodium perchlorate is slightly greater than the conductivity of sodium chlorate, because of its greater dissociation. The conductivities of sodium chlorate and sodium perchlorate are less than the conductivities of potassium chlorate and potassium perchlorate. Since the dissociations of the sodium salts are greater than those of the potassium salts, and the potassium cation has a larger mass and atomic volume than the sodium cation, it would be a difficult matter to explain the above fact without the solvate theory. The sodium ion is more hydrated in solution than the potassium ion, and must draw with it, through the solvent, a more complex hydrate, which necessarily decreases its velocity. It should be noted that sodium perchlorate crystallizes with one molecule of water.

Potassium perchlorate is dissociated to a greater extent than potassium chlorate, except at 0°. Its conductivity is at all temperatures higher than that of potassium chlorate for the corresponding dilutions.

Dissociations

With the single exception of potassium phosphate, dissociation decreases with rise in temperature, as we should expect from the Thomson-Nernst hypothesis and the relation pointed out by Dutoit and Aston. In the case of potassium phosphate, there is a marked increase in dissociation with rise in temperature except for the most concentrated solution. Contrary to the usual course of events, ionic complexes appear to be more rapidly broken down at a low temperature than at a high one. As the complex breaks down hydrolysis takes

place. It may be found that the increase is due to an abnormal exothermic heat of dissociation of this salt. It is evident from the results that the conductivity of the N/32 solution at 0° increases more rapidly with dilution than at any higher temperature.

The dissociations of salts of metals in the same group having a similar chemical composition are of the same order of magnitude. As a general rule, the sulphates in concentrated solutions are less dissociated than the corresponding nitrates and chlorides. This is probably due to the polymerization of the sulphates. Salts of metals in the second group are dissociated considerably less than salts of the alkali metals, under the same conditions of temperature and dilution. As a rule, the dissociation of any chloride, nitrate, sulphate, etc., decreases as the valence of its cation increases.

According to conductivity measurements, it is only the salts that are strongly hydrolyzed and hydrated that show any marked decrease in dissociation with rise in temperature. The sulphates of chromium and aluminium show a very marked decrease. It is probably due to the fact that with rise in temperature and dilution the polymers are rapidly broken down. If it were possible to measure the true μ_∞ value of these salts, the decrease in dissociation with rise in temperature, as measured by the conductivity method, would be much greater than that indicated by the tabulated results.

Temperature Coefficients

Temperature coefficients in conductivity units, as Jones and his coworkers have often pointed out, were found to increase with rise in temperature and increase in dilution. Ammonium acid sulphate presents a remarkable exception to this rule. Its coefficients not only decrease, but for a solution of a concentration $V = 512$ or less, and the temperature range 35°–65°, its coefficients are negative. In concentrated solutions and over the temperature range 35°–65°, chromium, aluminium and uranyl sulphates also showed decreasing temperature coefficients. Why the conductivity of the salt should begin to increase less

rapidly at these high temperatures than it does at a lower temperature is unknown.

Ammonium acid sulphate, for the concentrated solutions, shows but a very small increase in conductivity with rise in temperature. Its increase is greatest the lower the temperature range. If the conductivity of its 0.5 N solution increased with rise in temperature at the same rate as that for chromic nitrate, we would have at 65° a conductivity of over 600 instead of 235.5. The small increase in conductivity of the concentrated solutions indicates small hydrolysis and hydration. The depolymerization of the molecules must also be small. With increase in dilution some one of these factors, or, possibly, all of them act so as to increase greatly the conductivity with rise in temperature. In these dilutions temperature coefficients approaching more nearly to the normal coefficients are obtained. This points to the conclusion that the presence of a large number of unionized molecules are more capable of holding in check, with rise in temperature, the factors that ordinarily cause conductivity to increase with rise in temperature. The nature of sulphates in aqueous solution is not well understood, and merits closer and more elaborate study.

Large temperature coefficients are for the most part conditioned by hydration and hydrolysis. There two factors are evidently closely connected. It may be that water of hydration is more readily dissociated than water which is not in combination with the dissolved particles. The salts that are most strongly hydrated are, as a rule, the ones that are strongly hydrolyzed and most soluble. Jones and his coworkers[1] have already pointed out a number of relations existing between temperature coefficients of conductivity and the solvate theory of solution. The relations which they have discovered are confirmed by this work.

The remarkable increase in the temperature coefficients of conductivity of chromium and aluminium sulphates with rise in temperature and increase in dilution must attract attention. They finally reach values greater than those of any other salt

[1] Carnegie Institution of Washington, Publication No. 60, pp. 77–83.

studied. In dilute solutions, rapid depolymerization probably takes place with rise in temperature. The complex hydrates are readily broken down and hydrolysis increases. In concentrated solutions the effect of these factors with rise in temperature is very small.

Not much of interest can be deduced from the temperature coefficients in per cent. Jones[1] has pointed out that where $V = 8$ and the temperature range 25°–35°, the average value of the coefficient for a large number of widely different compounds is close to 2. Without an exception the temperature coefficients of conductivity in per cent. decrease with rise in temperature. Here, again, the coefficients of the sulphates are abnormal. Ammonium acid sulphate, chromic sulphate, uranyl sulphate and aluminium sulphate show negative coefficients in concentrated solutions. Those of chromium, aluminium and uranyl sulphates pass through a minimum. Ordinarily, a salt strongly hydrated and hydrolyzed shows a decided increase in the percentage temperature coefficients with increase in dilution. Those for salts not hydrated, hydrolyzed or polymerized are fairly constant.

SUMMARY

1. Some of the more important relations earlier pointed out by Jones and his coworkers, which the results obtained in this work confirm, are as follows:

Conductivity increases with temperature and dilution.

As a rule, temperature coefficients in conductivity units increase with rise in temperature. Salts strongly hydrated have large coefficients, those not strongly hydrated have small coefficients. The temperature coefficients are of the same order of magnitude for salts having approximately the same hydrating power. They increase with dilution, and the increase is greatest for those substances with large hydrating power.

With but one exception dissociation was found to decrease with rise in temperature.

Temperature coefficients in per cent. decrease with rise in temperature.

[1] Carnegie Institution of Washington, Publication No. 170, pp. 77–83.

2. Abnormal and striking relations appearing in many of the conductivity tables have been pointed out, and in most cases satisfactory explanations, based upon what we to-day know in regard to the nature of solution, could be offered.

3. A dehydrolytic time factor in the case of chromic salts was observed. It was pointed out that in purifying a chromic salt for conductivity work, it must not be heated to a temperature higher than that at which its conductivity is to be taken, since the dehydrolysis time factor persists for months.

4. Other salts readily hydrolyzed were tested for dehydrolytic time factors. It was concluded that in purifying such salts it is safe to heat their solutions up to temperatures not far from the temperature at which they would decompose.

5. The effect of the air conditions on the water correction was brought out in a quantitative way, and other suggestions made to improve the accuracy of conductivity measurements.

6. The influence of hydration, hydrolysis and polymerization on conductivity measurements has been discussed, and it is concluded that the Kohlrausch conductivity method is not a good one for measuring the dissociation of sulphates which are strongly polymerized, nor for measuring the dissociation of any electrolyte which is at the same time hydrated and hydrolyzed.

CHEMICAL LABORATORY
JOHNS HOPKINS UNIVERSITY
January, 1913

REVIEWS

SOIL CONDITIONS AND PLANT GROWTH. By EDWARD J. RUSSELL, D.Sc. (Lond.), Goldsmiths' Company's Soil Chemist, Rothamsted Experimental Station, Harpenden. With diagrams. Monographs on Biochemistry, edited by R. H. A. PLIMMER, D.Sc., and F. G. HOPKINS, M.A., M.B., D.Sc., F.R.S. London, New York, Bombay and Calcutta: Longmans, Green & Co. pp. viii + 168. Price, $1.50.

This is, probably, the most interesting and readable production in its line, since Johnson's "How Crops Feed" and "How Crops Grow." Written by the present Director of the famous Rothamsted Station and primarily for an English audience, it will nevertheless make a strong appeal to every one interested in the principles of agriculture, wherever they may be. It should have a wide field of usefulness.

It will appeal to the tyro because of the very attractive style in which the subject matter is presented, and because of the evident sincerity of the author, manifested strikingly in his judicial attitude toward the polemics with which the literature is fairly rife. To the expert the book will appeal, not only for the qualities just mentioned, but more for its suggestiveness.

Page after page will present paragraphs which, if they do not incite direct disagreement with the author, will at least suggest argument. There is a strong personality evidenced. An adequate review of the monograph would entail the writing of another (and perhaps larger) book. Consequently the present reviewer feels justified in calling particular attention to a few points only, while recording his judgment that Dr. Russell's book is of far more than ordinary scientific merit as well as interest.

Throughout the book and especially in the discussion of biological phenomena there is a clear recognition that all soil phenomena involve continuous changes. Yet, inconsistently, in discussing the "law of the minimum," "dominant factors," soil exhaustion and soil analyses there is evident an implicit assumption that the mineral factors in a soil do not change. In other words, a convincing array of data is marshalled showing that soil phenomena are all essentially dynamic in character, yet the discussion is mainly from a static point of view. It will be readily admitted by every one that, in any particular case, there may be a dominant factor or group of factors; but it does seem that the time has come when more progress would be made by recognizing, as a fundamental principle, that crop production is always the resultant of many variables, every one of which is interdependent with every other, and in consequence apparently "dominant" factors are of no more actual importance than each and every other factor.

Certain omissions from the discussion are surprising. One would expect, for instance, a discussion of the actual amounts of mineral ingredients (plant food) taken from and returned to the soil by plants during growth, the content at different stages of growth, and some notice of the work of Wilfarth, Römer and Wimmer,[1] and LeClerc and Breazeale.[2] Again, while one may agree with the author that the development of soil physics is lamentably unsatisfactory (pp. 85 *et seq.*), it does seem that a better case could be made for it. The significance of Mitscherlich's observations on the heat of wetting, the correlation of physical properties with the moisture con-

[1] Landw. Vers. Sta., **63**, 1 (1905).
[2] Year Book, U. S. Dept. Agr., **1908**, pp. 389–402.

tent of the soil, and the distribution of the rainfall in the soil are among the subjects which one might expect to find discussed and upon which it would be desirable to have Dr. Russell's views.

The discussion of soil colloids is not satisfying and creates the impression that they are a useful invention for bolstering otherwise troublesome arguments, rather than entities with which one can actually experiment. This is due in large part, of course, to the very hazy ideas generally prevailing regarding colloids and colloidal properties. Admitting that mineral colloids exist in the soil (for which no satisfactory evidence is given) it is certainly going too far to ascribe to them alone the adsorptive properties of the soil mass (pp. 54–58) as it is to claim from Way's work that "fixation" is essentially metathesis. The rather large body of conflicting evidence does not receive adequate attention.

The evident intention of fairness and the courtesy with which Dr. Russell has presented views with which he is not in accord have been noted above. However, a far from accurate presentation is given of the reviewer's own opinions regarding the composition and concentration of the soil solution and its relation to the solid components of the soil on the one hand and the growing plant on the other. This matter has been discussed quite fully in the reviewer's own recent book, and more recently been restated in another form,[1] and cannot be discussed here. But as one who has had a considerable part in the development of what Dr. Russell designates the "Whitney School," the reviewer feels obliged to record that his views are not accurately described by the references and discussion in the present book. For instance, the Whitney School(?) holds much the same attitude towards the hypothesis of toxic organic plant excreta that Dr. Russell holds toward the bacteria-protozoa theory, i. e., it may be "one of the factors....limiting....fertility in ordinary soils" (p. 118). It is far more important to recognize that organic substances exist in soils, sometimes injurious to plants, whatever may be their origin, by excretion, by cell sloughing or by secondary decomposition of organic débris.

On the whole the discussion of chemical principles involved in soil phenomena is rather meager. But analytical data are frequently given and the time-worn subject of soil analysis comes in for further discussion. It appears that, on the whole, Dr. Russell thinks that sometimes it might be worth while, but the candid reader will probably find it hard to see why. A strong argument is advanced for soil surveys under governmental auspices.

[1] Proc. 8th Int. Cong. Appl. Chem., Vol. 15.

The text is unusually free from mechanical and typographical errors, though a few were noted. Valuable (p. 24) should be variable. Hydrolysable (p. 31) will grate on some ears. A selected bibliography and reference list is a very valuable feature of the monograph, and there is also a satisfactory subject index.

FRANK K. CAMERON

TRAITÉ DE METALLOGRAPHIE. Par FÉLIX ROBIN. Préface de M. F. OSMOND. Paris: Libraire Scientifique A. Herman et Fils. 1912. pp. 464. Price, Fr. 30.00.

The author has produced a book which is a curious combination of much that is good and appropriate to the proper study of metallography, and much that has little, if any, bearing on the subject as it is ordinarily understood. He has included chapters on certain subjects such as hardness, compression figures, micro-chemical analysis, which are usually more appropriately treated in books on mineralogy. There is further a rather remarkable blending of material which can be spoken of as academic and practical. The practical side of the subject has been much more satisfactorily and extensively developed than is customary and it will be welcomed on this account, although the material is not so classified as to be easily found. The equilibrium diagrams are both good and bad. Some represent the latest development while others are quite ancient. Some of the more recent developments in diagrams are taken from German sources without changing the German wording; others are old French diagrams which are reproduced in spite of the fact that more reliable data were available. As usual with French books there has been little tendency to give full bibliographic references, but in some respects this is an improvement upon the average. The photographic reproductions are many and very good, and some of the composite photographs excellent.

A résumé of chapter headings would give one little idea of what the book actually contains. The author treats inadequately the history of the science and the subject of equilibrium diagrams; gives a good idea of the preparation and examination of specimens for microscopic study; discusses fully and satisfactorily the micrographic constituents of steels and irons, with considerable comment upon the effect of work, impurities, etc., upon the physical properties. Alloy steels, the brasses, bronzes, and other copper alloys are discussed, and there is a chapter on slags.

The book will be of most service to those interested in the metallography of steels.

HENRY FAY

A DICTIONARY OF APPLIED CHEMISTRY. By SIR EDWARD THORPE, C.B., LL.D., F.R.S., Emeritus Professor of Chemistry, Imperial College of Science and Technology, South Kensington, London, assisted by Eminent Contributors. Revised and enlarged edition in five volumes. Vol. III, Gr-Oils. With illustrations. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. viii + 789. Price, $13.50.

The first two volumes of the new edition of this very valuable work have been recently reviewed in these columns;[1] and it is gratifying that the publishers are making such rapid progress with this new issue. No change in the plan or arrangement of subject matter is noted from the scheme adopted for the two volumes already issued, and as before many prominent names are found in the list of some thirty-six contributors.

Within the alphabetical range included in this volume, there are one hundred and forty new topics not included in the old edition. Of these the following are some of the more important: Guanidine; Gypsum; Haematite; Halogen-acetic Acids; Helium; Histidine; Hydrastine; Hydrolysis; Indanthrene Dyes; Indene; Indigo, Artificial, and Indigoid Dyestuffs; Indoxyl Compounds; Invertase; Ionium; Iridium; Isoprene; Ivory; Ketenes; Krypton; Lacquer; Lactones; Lanthanum; Lard; Lipase; Liquefaction of Gases; Liqueurs and Cordials; Lutecium; Maize and Maize Oil; Malonic Acid; Maltase; Martensite; Meat Extract; Mercaptans; Mercerizing; Metallography; Neat's Foot Oil; Neodymium; Neon; Nigrisin; Niton; Nitranilines; Nitriles.

About seventy topics included in the old edition have been rewritten and much enlarged, the more important being as follows: Graphite (but artificial graphite receives scant notice); Guaiacol; Gums, (including new matter on Suakin, Morocco, Aden and Australian or Wattle gums); Hydrazines; Hydrazones; Hydrogen Peroxide; Hypoxanthine or Sarcine; Indigo, Natural; Indium; Iron; Ketones; Lactic Acid; Lactones; Leucine; Lithium; Logwood; Lubricants; Margarine; Matches; Methyl; Molybdenum; Monazite; Naphthalene; Nitrogen, Atmospheric, Utilization of; Nitric Acid, Manufacture of; Oils, Essential; Oils, Fixed.

The references to original papers and general tenor of these articles appear to bring the subjects up to about the end of 1910. The rare gases, Helium, Krypton, and Neon, and also the recently discovered Niton, are considered in interesting paragraphs. An excellent digest is given of the principles of Hydrolysis, as illustrated by the ordinary types, viz., hydrolysis of metallic salts, of esters, of acyl derivatives (acid chlorides, amides, etc.), of complex carbohydrates (di- and polysaccharoses and glucosides); also a discussion of the effect of neu-

[1] THIS JOURNAL, **48**, 191, 259.

tral salts in hydrolytic reactions, of enzyme action in inducing these processes, and finally those reactions in which alcohols play similar parts. A brief article on Indanthrene and the new class of "vat dyes" grouped with it affords information on the methods of preparation, constitution and properties of these valuable colors. Artificial Indigo, and the related Indigoid Dyestuffs, occupies about five pages; here is also shown the far-reaching consequences of the manufacture of this new material upon the well-established processes of production and application of the other artificial dyestuffs.

About eight pages are given to a discussion of the Lactones, the methods of preparing them, with many structural formulas, the properties of the several classes of lactones, and special consideration of a few of the important ones, such as *meconin*, *coumarin*, *umbelliferone*, *daphnetin* and *aesculatin*. Under the topic Lard are found the definitions of the various brands of edible lard, as established by the Rules of the Chicago Board of Trade; also the mode of preparation, properties and uses of each brand. A paragraph is also devoted to Lard Substitutes.

The topic of Lead includes a subsection devoted to the Lead Compounds Used in the Arts, in which is a good description of White Lead making by the Dutch-English method, but the newer, more rapid methods, such as the Carter process, receive meager mention, while the old, generally abandoned Milner process is given more than a column. Among white lead substitutes, lead sulphate produced from furnace fume is described as Hannay's White Lead; the product appears to be essentially the same as the "sublimed white lead" made by the Picher process. It is surprising that no reference is made to the legislation lately enacted by various countries, restricting or even prohibiting (in France since 1910) the manufacture or use of white lead.

The Liquefaction of Gases gives an excellent summary of the work of the pioneers in this field: beginning with the comparatively little known studies of "gases" and "vapors" by van Helmont, Boerhaave, Dalton, Monge, Clouet and Northmore, previous to 1806, next follows Faraday's important work in 1823 and 1845, Andrews' in 1869 and 1876 and van der Waals' in 1879. The liquefaction of the "permanent" gases, oxygen and carbon monoxide, by Pictet and Cailletet in 1877 led to experiments by Wroblewski, Dewar and others, and finally in 1895 Hampsen and von Lindé devised methods of "self-intensive" refrigeration, and produced liquid air in large quantity. Many references to original publications are given. Under Meat Extracts is an interesting sketch of Liebig's connection

with the industrial manufacture of this material. The article also includes the methods of testing and analysis of meat extracts. Metallography fills some twenty-one pages, and two full-page plates are included, showing the micro-structure of pure metals and alloys. Typical cooling "curves" and equilibrium diagrams of various classes of alloys, e. g., copper-nickel, copper-zinc, lead-tin, etc., are explained; deformation, fracture, and fatigue in metals are also considered.

In the chapter on Iron a sketch of a modern blast furnace has been included, and the new special steels containing nickel, chromium, aluminium, tungsten, and rarer elements are considered; also the Talbot steel process. Leather is mainly devoted to the old vegetable tannage processes, while chrome tannage, so important in this country, receives but a few lines with no adequate description. Nor is much consideration given to the replacement of hand labor in the beam house by machines, nor to the devices for accelerating the tanning process. And the use of organic acids, such as formic and lactic, for deliming hides and skins is barely mentioned. But the methods of analysis of tanning materials receive considerable attention.

Under Matches the list of paste compositions, and of patent applications for match machinery, of the old edition have been eliminated, and an illustrated account of the manufacture as conducted in the works of Bryant and May, Ltd., of London and Liverpool, is included. Many of these illustrations are too small to add materially to the value of the article. All European countries and Japan have adopted laws prohibiting, or at least closely regulating, the use of white or yellow phosphorus in matches. One reads further, "Only in the United States is there no legislation relating to the manufacture or use of matches made with white or yellow phosphorus." It is stated that the common double-tip match used here contains as much as 20 per cent. of white phosphorus, and generates 40–50 per cent. more phosphorus oxide vapor during the process of manufacture than does the ordinary match. Also it appears that the "warmth and humidity of the American climate increase the danger to the workers."

The longest contribution in the volume is that on Naphthalene and its derivatives, comprising 101 pages. Copious references to original literature make this valuable in the organic industrial field.

A good account of the Lindé method of obtaining nitrogen from the air, with a diagram of the apparatus, opens the important subject of Nitrogen and its compounds. The Utilization of Atmospheric Nitrogen, which has assumed such import-

ance since the appearance of the first edition of the work, is excellently presented, and illustrated by numerous diagrams and views in the various factories. The manufacture of calcium cyanoamide (nitrolim), cyanides, ammonia (Haber's process) and nitric acid by the Birkeland-Eyde, Schoenherr, and Pauling methods are included. The Manufacture of Nitric Acid (from sodium nitrate and sulphuric acid), by Professor Edward Hart of Easton, Pa., is the only contribution to this volume from America. In this are given the latest devices for carrying on the process, each illustrated by a diagram.

As in the preceding volumes, the care exercised in editing and publishing has maintianed the high standard of the work.

F. H. THORP

DIE INDUSTRIE DER STEINKOHLENTEERS UND DES AMMONIAKS. Von DR. G. LUNGE und Dr. H. KÖHLER. Fünfte gänzlich umgearbeitete Auflage. Erster Band: Steinkohlenteer. Mit 354 eingedruckten Abbildungen. s. xviii + 1040. Preis: geh., M. 29.00; geb., M. 30.50. Zweiter Band: Ammoniak. Mit 163 Abbildungen im Text und auf 6 Tafeln. s. xii + 476. Preis: geh., M. 15.00; geb., M. 16.50. Neues Handbuch der chemischen Technologie (Bolley's chemische Technologie, dritte Folge), herausgegeben von Dr. C. ENGLER, wirkl. geh. Rat und Professor an der Technischen Hochschule Friedericiana in Karlsruhe. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912.

The fourth edition of this standard work appeared in 1900, since which time the great development of the by-product coke oven has occurred and in consequence the coal-tar and ammonia industry has not only enormously developed, but has widened greatly in its scope. As against 702 pages in the fourth edition of the volume on coal tar, 1040 pages are now devoted to this subject and the 323 pages of the earlier volume on ammonia have grown to 476 pages in the edition now published.

Nor does this consist simply of additional matter, supplementary to the old. The authors state that, as they wished to discuss the new material with proper fullness, they have cut out much of the description of older processes and referred the reader, whenever it seemed necessary, by a note to the 4th edition.

The first considerable expansion of the subject matter is found in the section on the production of tar as a by-product in the manufacture of coke. Instead of 49 pages, which were given in the previous edition, we have now 107 pages. In this we find a very full and detailed account of the newer forms of by-product ovens such as the Semet-Solvay, the several forms of the Otto oven, the Koppers, the Brunck and the Coppeé ovens. What is of great interest is the account of the development of the extraction of benzene from coke-oven gases which has revolutionized the benzene industry and made possible

many additional utilizations of it other than in the color industry. Thus in 1908, the German benzene production amounted to 90,000 tons, of which 80,000 tons were extracted from coke-oven gases and 10,000 tons from coal and coke-oven tars. England, during the same year, produced 35,000 tons of benzene, chiefly from coal tar, France 13,000 tons and Belgium 6,000 tons.

Of course, it is in Germany that the by-product coke oven has developed most generally, so that at the present time 80 per cent. of German coke ovens are by-product ovens, from which tar and ammonia are collected; Belgium follows closely with 70 per cent. of its ovens by-product ovens, while in England and the United States the proportion has only risen to 16.6 per cent. The manufacture of water-gas tar and oil-gas tar, both relatively newer products, is quite fully described and their respective characters as compared with gas-retort tar discussed. In this connection, tables of comparative analyses of tars of various types, submitted with a paper prepared by the late Dr. H. W. Jayne for the London International Congress of Applied Chemistry in 1909, are given.

Among the uses for coal tar as such, we find described in this edition the treatment of roads and the production of a tar-macadam coating for roads to allay or do away with the dust nuisance. This has been extensively practiced in the last ten years in France and in England and to some degree in Germany. The only reference to the utilization of tar for the improvement of roads in the United States is the statement on the authority of J. D. Pennock that in 1903 16,000 tons of tar were so used. The use of materials like "Tarvia," a coal-tar preparation for road treatment, and of California asphaltic residuums has, however, attained very large proportions in this country.

As might be expected, the section on the analysis and valuation of the tar samples is much enlarged and improved and recent methods are described and illustrated. As an example of this, we would call attention to the discussion of the question of "free carbon" in tar and the importance of its correct determination.

The use of coal-tar pitch as a binder in the manufacture of coal briquettes, which has become a very large industry in Germany, Belgium and France, is described and illustrated and its importance indicated by statistical tables.

The use of heavy or so-called creosote oil for the preservation of wood has advanced greatly in the past decade and this subject is very fully treated in the volume before us, the Rüping process, which has found great acceptance in Germany, being

very fully described and illustrated. By this process, while the cell walls become thoroughly coated with the creosote oil, the excess of oil is forced out by air which has been compressed in the center of the timbers and much less oil is required than by the older process.

The progress of wood preservation in the United States is also noted and its status as late as 1910 reviewed.

The statistics of coke and coal-tar production throughout the world are brought down almost to the date of the issue of the work by notes in the appendix.

Volume II on Ammonia has not only grown in size, as noted before, but contains much that is radically new, representing the important synthetic work in this line that has been accomplished in the past decade or so. Thus we have a brief mention of Haber's process for the synthesis of ammonia from nitrogen and hydrogen in the presence of catalyzing agents, which is now being developed by the Badische Anilin- und Soda-Fabrik, a fuller account of which was given by Prof. Bernthsen at the late Congress of Applied Chemistry in New York. We have next the synthesis of ammonia through the intervention of the nitrides and here a very full account of Serpek's very successful process with aluminum nitride is given, whereby pure ammonia and pure alumina are manufactured from bauxite. We have also the processes for the production of ammonia by the intervention of cyanides and of cyanoamide, now so extensively manufactured by Frank and Caro's process.

This new edition also devotes a large space to the subject of liquefied ammonia, which has assumed far greater importance commercially than was the case at the time the earlier edition appeared. This section is especially well illustrated, moreover, showing the mechanical side of the liquid ammonia industry, its compression, its storage and its transportation.

We must not fail to note in conclusion that the German type of the older edition has given place to the Latin characters and that the book is both printed and illustrated with that perfection of mechanical detail so well known in the scientific books of Vieweg and Son.

SAM. P. SADTLER

DAS HYDROSULFIT. Teil II. Anorganische, organische und technische Chemie des Hydrosulfits. Von Dr. KARL JELLINEK, Privatdozent an der Technischen Hochschule zu Danzig. Mit 2 Kurven. Sonderausgabe aus der Sammlung chemischer and chemisch-technischer Vorträge, begründet von F. B. AHRENS, herausgegeben von Prof. DR. W. HERZ, Breslau. XVIII Band, 1–6 Hefte. Stuttgart: Verlag von Ferdinand Enke. 1912. pp. viii + 230. Price, M. 9.00.

The first volume, dealing with the theoretical chemistry

of hydrosulphite, has already been reviewed.[1] The second volume should recommend itself most highly to all who are interested in any way whatever in hydrosulphite chemistry. The subject is treated in a clear and comprehensive manner as follows: I. Inorganic Chemistry, pp. 1–78. II. Organic Chemistry, pp. 79–125. III. Technical Preparation of Hydrosulphite and its Derivatives, pp. 125–168. IV. Technical Applications of Hydrosulphite and its Derivatives, pp. 169–208. The last 22 pages of the book contain a list of commercial products, the bibliography complete to March 1912, a list of German patents, and a subject and author index.

No details of technical methods of preparation, etc., have as yet been published, and the author is therefore forced to rely upon patent specifications and claims. He estimates that the annual German hydrosulphite output has a value of several million marks. The technical price is about 2 marks per kilo.

WILLIAM C. BRAY

CHEMISCH-TECHNISCHES PRAKTIKUM. Uebungsbeispiele aus der chemisch-technischen Analyse für Studierende an technischen Hochschulen und Universitäten. Von DR. ING. WILHELM MOLDENHAUER, Privatdozent für Chemie an der Technischen Hochschule zu Darmstadt. Berlin: Gebrüder Borntraeger. pp. vii + 206. Price, M. 6.80.

In this work, which is intended for use in technical high schools and universities, the author has taken as examples of analytical processes used in technology such cases as have a practical bearing and are encountered in the daily work of a technical chemist. The methods are described in sufficient detail to enable one to carry out the determination without difficulty and the reactions involved and the uses and properties of the substances are often discussed. An idea of the scope of the work can be obtained from a list of some of the subjects treated: Coal, water, illuminating gas, sulphur, saltpeter, soda, fertilizers, iron ores, zinc ores, oils, fats, soaps, glycerol, etc.

J. E. G.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By GEORGE SENTER, D.Sc. (Lond.), Ph.D., Lecturer on Chemistry at St. Mary's Hospital, University of London, Lecturer on Physical Chemistry, Cass Technical Institute, Oldgate, E. C. London; Methuen & Co., Ltd.; New York: D. Van Nostrand Co. 1911. pp. x + 583. Price, $1.75.

The author has, in this text book of nearly 600 pages, given us a clearly written descriptive inorganic chemistry in which the more important of the modern theories of chemistry, such as the Principles of Chemical Equilibrium, the Determination of Molecular Weights in Solution, Electrolysis and Electrolytic

[1] THIS JOURNAL, 48, 98 (1912).

Dissociation are introduced at an early stage and their applications illustrated in the rest of the book. Owing to the size of type used it has been possible to enter very fully into the chemistry of the elements and compounds, and produce an excellent book for students in inorganic chemistry. J. E. G.

ELEMENTARY CHEMICAL THEORY. By J. M. WADMORE, M.A. New York: D. Van Nostrand Co. 1912. pp. 275. Price, $1.50.

"Being unable to find a suitable elementary text book on Theoretical Chemistry the author has, with some reluctance, added to the already large number of text-books on elementary substances." He has, however, given us a very clear and logical treatment of the subject, presenting only those features which will enable the student to grasp the results of the work in various lines without being completely lost in the maze of details whose relative value and bearing he is not yet able to appreciate. A student who has studied chemistry for a year should find this book interesting and helpful. J. E. G.

DIE ANALYSE DER SELTENEN ERDEN UND DER ERDSÄUREN. Ceriterden, Yttererden, Zirkonerde und Thorerde, Titansäure, Niobsäure und Tantalsäure. Von PROF. DR. R. J. MEYER, Privatdozent an der Universität Berlin, und DR. O. HAUSER, Privatdozent an der Techn. Hochschule Berlin. Mit 14 Abbildungen und 31 Tabellen. Die Chemische Analyse. Sammlung von Einzeldarstellungen auf dem Gebiete der chemischen, technisch-chemischen und physikalisch-chemischen Analyse. Herausgegeben von DR. B. M. MARGOSCHES, Privatdozent an der Deutschen Technischen Hochschule Brünn. XIV–XV. Band. Stuttgart: Verlag von Ferdinand Enke. 1912. pp. 320. Price, M. 10.

This book is a very valuable contribution to the literature of the chemistry of the rarer elements, concerned as it is with the analytical chemistry of the rare earths and rare earth acids. The joint consideration of these two groups is most instructive because of their intimate association in nature in many minerals.

The reputation of the authors gives one much confidence in the character of the work, and the selection of material is excellent.

The importance of spectrum analysis is wisely emphasized and the frequent tabulation of the chief lines in the arc and spark spectra, as well as the clear plates showing absorption spectra, will prove most valuable to the student in this field of research.

Some important work by American chemists, such as the recent work of Hunter upon elementary titanium and of James upon the rare earths, might have been added with advantage.

PHILIP E. BROWNING